UPPER AND LOWER BOUNDS TO EIGENVALUES BY THE PARTITIONING TECHNIQUE

By

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INTRODUCTION

The quantum theory of atoms, molecules and solids, in its non-relativistic formulation, stems out of the time dependent Schrödinger equation:

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

and from its time independent form for the stationary states:

$$H\Psi_n = E_n \Psi_n \quad .$$

The Hamiltonian H consists of the kinetic energy operator plus the potential energy operator, constructed with the well-known prescriptions $x \rightarrow x$, $p_x \rightarrow -i\hbar \frac{\partial}{\partial x}$. Thus, for a system of N particles, with masses m_i, charges g_i and interacting through coulombic potentials, the Hamiltonian may be written:

$$H = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i<j}^{N} \frac{g_i g_j}{r_{ij}} \quad .$$

It is a truism to say that the Schrödinger equation very seldom may be solved exactly. In fact, the vast literature in this field during the last forty years contains a large variety of approximate methods that have and are being used to solve this complicated eigenvalue problem. As exact solutions are not easily available, it is desirable that the approximate methods provide estimates of the error,

namely, upper and lower bounds to the eigenvalues E_n, and criteria of accuracy for the approximation to the eigenfunctions Ψ_n. The latter will be of two types: local, and in some average sense to be defined in each case.

The approximation methods used can be classified as falling into two types: variation and perturbation. Variation methods provide upper bounds to eigenvalues through the solution of secular equations. They do provide, too, some estimates of the overlap of the solutions of the secular equation with the exact eigenfunctions. By overlap we mean the integral $\int \Psi_n^* \Phi_n (dv)$. It is possible to obtain lower bounds from variational solutions by additional computation and additional information: in Temple's method[1] the computation of the expectation value of H^2 and the knowledge of E_1, the first excited state of H is needed to compute a lower bound to the ground state, E_o. Similarly, the knowledge of E_1 provides a bound for the overlap of Ψ_o with an approximate Φ_o in Eckart's method[2]. Lower bounds from variational methods can be constructed by the technique of intermediate problems, of which Weinstein, Aronszajn, Bazley and Fox[3], are mainly responsible.

Perturbation methods can provide upper and lower bounds to the quantities being approximated, yet this is not true for all perturbation schemes.

The partitioning technique, developed by Löwdin[4], provides a synthesis of different perturbation approaches and relates them to variation methods.

Through use of a bracketing theorem, upper and lower bounds to the eigenvalues and local and norm errors for the wave function can be

estimated. This has been extensively discussed by Löwdin in his series on perturbation theory[4].

In this dissertation we try to explore some of the aspects of partitioning technique combined with operator inequalities and the techniques of inner and outer projections. A review of the mathematical background is presented in Chapter I, which indicates tools to be developed further. In Chapter II we explicitly relate the widely used Temple formula with a specific approximation to the partitioning expressions. By use of successive partitioning technique, in Chapter III, we establish the connection with Feenberg's[5] perturbation schemes. This derivation emphasizes the conceptual relationships between the perturbation schemes. The combination of the inhomogeneous equation approach of Dalgarno, Hirschfelder et al[6] with partitioning schemes proves to be very fruitful in formulating explicit solutions to the intermediate problems in Chapter V. Chapter IV contains a new derivation of upper and lower bounds to even orders of perturbation series, obtained originally by Prager and Hirschfelder[7] through analogy with electromagnetic theory. Variation principles for excited states, via perturbation theory, are obtained in this fashion too. The approach is geometrical in nature and follows the work by Synge[8]. Chapter VI discusses a transformation of the Schrödinger eigenvalue problem which, for one-electron problem yields a complete, discrete spectrum as shown by Hylleraas[9] and Schrödinger[10]. For many-electron problems, the transformation allows the use of the operator inequalities reviewed in Chapter I thus yielding new lower bound formulae. In a simple-minded approach for H_2^+ this transformation proved to be very effective[11],

as compared with the Bazley and Fox method. Several ways of computing lower bounds appear to be feasible, including the application to molecular systems by the construction of an Hermitian positive operator.

Some numerical aspects of partitioning derivatives of the bracketing function, etc., in connection with the He atom are discussed in Appendix I.

The discussion will be based on the areas of future research and applications that are suggested by the results presented in this dissertation.

CHAPTER I

MATHEMATICAL BACKGROUND

1.1. Partitioning Technique

In what follows we present a review of the aspects of partitioning technique pertinent to our work. For a more detailed account see the papers by Löwdin on perturbation theory, which will be referred to as PTI - PTXI.[4].

Consistent with the aims of this study, which is to exploit the operator formalism in solving the Schrödinger equation, we will discuss partitioning in operator form. The object of study is the time independent eigenvalue problem:

$$H\Psi_n = E_n\Psi_n \quad . \tag{1.1}$$

We seek upper and lower bounds to the E_n and well defined approximations to the Ψ_n. We shall restrict our attention to bound states, although the formalism allows the treatment of scattering states as well as time dependent problems.

The building blocks of the theory are an energy variable $\mathcal{E}$, and a reference space of linearly independent functions. For our present purpose it is enough to make the reference space one-dimensional, i.e., we consider a reference function Ψ, assumed to be normalized. Löwdin[12] discussed the multidimensional reference space, and applications have been made[13] and are under progress.

The projection operator associated to ψ: $O = |\psi\rangle\langle\psi|$ satisfies the usual relations

$$O^2 = O; \quad O^+ = O; \quad \mathrm{Tr}(O) = 1 \quad . \tag{1.2}$$

The orthogonal complement to ψ is characterized by a projection operator P with

$$P^2 = P; \quad P^+ = P; \quad P = 1 - O; \quad PO = OP = 0 \ . \tag{1.3}$$

Given the reference function and the energy variable $\mathcal{E}$, we introduce the reduced resolvent associated with (1.1):

$$T = P[\alpha O + P(\mathcal{E} - H)P]^{-1}P \tag{1.4}$$

where α is any constant different from zero. The properties of T give a clue to its nature: it is the inverse of $\mathcal{E} - H$ in the subspace projected by P. $P(\mathcal{E} - H)P$ itself has no inverse, because it is zero in the subspace O. By adding αO to $P(\mathcal{E} - H)P$ we may safely construct the inverse, and then project out the desired component in P. If this is to be consistent at all, T should be independent of α:

$$\frac{\partial T}{\partial \alpha} = P[\alpha O + P(\mathcal{E} - H)P]^{-1}O[\alpha O + P(\mathcal{E} - H)P]^{-1}P = 0 \ . \tag{1.5}$$

Notice that T "blows up" whenever $\mathcal{E}$ is equal to one of the eigenvalues of PHP. The properties that make T interesting are:

$$OT = TO = 0, \quad PT = TP = T, \quad T = T^+ \ . \tag{1.6}$$

If one multiplies by P the following expression:

$$[\alpha O + P(\mathcal{E} - H)P][\alpha O + P(\mathcal{E} - H)P]^{-1} = 1 \ ,$$

the important result

$$P(\mathcal{E} - H)T = P \tag{1.7}$$

follows. It is customary to use the symbolic notation

$$T = \frac{P}{\mathcal{E} - H} \tag{1.8}$$

although (1.4) is meant by it.

A trial wave function $\Psi_{\mathcal{E}}$ associated with ψ and $\mathcal{E}$ is defined by:

$$\Psi_{\mathcal{E}} = \psi + TH\psi = (1 + TH)\psi = \psi + \phi_{\mathcal{E}} \quad . \tag{1.9}$$

This definition implies the adoption of intermediate normalization:

$$\langle \psi | \Psi_{\mathcal{E}} \rangle = \langle \psi | \psi \rangle + \langle \psi | TH\psi \rangle = 1 + \langle \psi | PTH\psi \rangle = 1 \tag{1.10}$$

$$\langle \Psi_{\mathcal{E}} | \Psi_{\mathcal{E}} \rangle = 1 + \langle \psi | HT^2H | \psi \rangle = 1 + \langle \phi_{\mathcal{E}} | \phi_{\mathcal{E}} \rangle \quad .$$

If $\langle \phi_{\mathcal{E}} | \phi_{\mathcal{E}} \rangle$ exists, $\Psi_{\mathcal{E}}$ belongs to the discrete spectrum, otherwise, it is a scattering state.

We now consider the expression $(H - \mathcal{E})\Psi_{\mathcal{E}}$. First notice that $\Psi_{\mathcal{E}}$ is a solution of the Schrödinger equation in the subspace P:

$$P(H - \mathcal{E})\Psi_{\mathcal{E}} = P(H - \mathcal{E})\psi + P(H - \mathcal{E})TH\psi$$

$$= PH\psi - PH\psi = 0.$$

Therefore:

$$(H - \mathcal{E})\Psi_{\mathcal{E}} = (O + P)(H - \mathcal{E})\Psi_{\mathcal{E}} = O(H - \mathcal{E})\Psi_{\mathcal{E}}$$

$$= \psi\langle\psi|H - \mathcal{E}|\Psi_{\mathcal{E}}\rangle = \psi(\langle\psi|H|\Psi_{\mathcal{E}}\rangle - \mathcal{E}) \quad .$$

Denote $\langle\psi|H|\Psi_{\mathcal{E}}\rangle$ by $\mathcal{E}_1$. It is apparent that $\Psi_{\mathcal{E}}$ satisfies an inhomogeneous equation:

$$(H - \mathcal{E})\Psi_{\mathcal{E}} = (\mathcal{E}_1 - \mathcal{E})\psi \tag{1.11}$$

If $\mathcal{E}_1 = \mathcal{E} = E$ it turns out that $\Psi_{\mathcal{E}}$ is an eigenfunction corresponding to the eigenvalue E. Obviously, for an arbitrary value of $\mathcal{E}$, $\mathcal{E}_1 \neq \mathcal{E}$, yet the relation between $\mathcal{E}_1$ and $\mathcal{E}$ is of particular significance:

$$\mathcal{E}_1 = \langle\psi|H|\Psi_{\mathcal{E}}\rangle = \langle\psi|H + HTH|\psi\rangle = f(\mathcal{E}). \tag{1.12}$$

Consider the slope of the function $\mathcal{E}_1 = f(\mathcal{E})$:

$$\frac{d\mathcal{E}_1}{d\mathcal{E}} = \langle\psi|H\frac{\partial T}{\partial\mathcal{E}}H|\psi\rangle = -\langle\psi|HT^2H|\psi\rangle$$

$$= -\langle\phi_{\mathcal{E}}|\phi_{\mathcal{E}}\rangle < 0. \tag{1.13}$$

Therefore, for values of $\mathcal{E}$ in the discrete spectrum region, $\frac{d\mathcal{E}_1}{d\mathcal{E}}$ is negative. This leads to the bracketing theorem, which holds for all iteration schemes of the type $\mathcal{E}_1 = f(\mathcal{E})$ with $f'(\mathcal{E}) < 0$. See PTI.

Let E be an eigenvalue of H, i.e., $\mathcal{E}_1 = f(\mathcal{E}) = E = \mathcal{E}$. Consider a pair of values $\mathcal{E}$, $\mathcal{E}_1$. We can write:

$$\mathcal{E} = E + \epsilon \; ; \; \mathcal{E}_1 = E + \epsilon_1 \quad . \tag{1.14}$$

ϵ_1 and ϵ not necessarily small. Then it follows:

$$\mathcal{E}_1 = E + \epsilon_1 = f(\mathcal{E}) = f(E + \epsilon) = f(E) + \epsilon f'(E + \theta\epsilon)$$

which reduces to:

$$\epsilon_1 = f'(E + \theta\epsilon) \quad . \tag{1.15}$$

We have used Lagrange's mean value theorem, and $0 \leq \theta \leq 1$. As $f'(\mathcal{E})$ is negative, ϵ and ϵ_1 have different sign, and the bracketing theorem is proved: $\mathcal{E}_1$ and $\mathcal{E}$ bracket one eigenvalue E to H. (See Fig. 1.) Clearly one may bracket several eigenvalues to H.

An immediate application of the bracketing theorem follows from (1.12) by setting $\mathcal{E} = -\infty$. Then $\mathcal{E}_1 = \langle\psi|H|\psi\rangle$ is an upper bound to the ground state eigenvalue E_o, a result that follows from the variational principle otherwise.

The curve $\mathcal{E}_1 = f(\mathcal{E})$ is interesting. The eigenvalues are the crossings of $\mathcal{E}_1 = f(\mathcal{E})$ with the line $\mathcal{E}_1 = \mathcal{E}$. The curve has negative slope everywhere in the bound state region and it has vertical asymptotes for $\mathcal{E}$ equal to the eigenvalues of PHP $\equiv \overline{H}$, which we shall label by $\overline{E}_i$. (See Fig. 2.)

The conventional perturbation schemes stem out of power series expansions of (1.11), and provide approximations to E and Ψ. The aim of the present method is to study the interval $(\mathcal{E},\mathcal{E}_1)$ instead of the special points E. This is significant for two reasons: Upper and lower bounds to the eigenvalues are obtained. Further, the trial wave function satisfies the Schrödinger equation with a local accuracy $(\mathcal{E}_1 - \mathcal{E})$, as indicated by (1.11) and with an average accuracy

$$||(H - \mathcal{E})\Psi_{\mathcal{E}}|| = \mathcal{E}_1 - \mathcal{E} \tag{1.16}$$

which should be useful in the study of properties other than energy.

The following digression is not out of place here. It was pointed out by Synge[8] that many boundary problems of mathematical physics can be stated in the form "It is required to find the intersection of two orthogonal subspaces of a function space." The usual method of setting up an infinite process (power series solutions) has the required intersection as a limit. The individual terms do not satisfy in general the boundary conditions, yet they are satisfied by the limit. An example of this would be Fourier-type description of the solution of a boundary value problem. It is quite clear that the partitioning scheme implies two orthogonal subspaces, in a somehow different sense from Synge's, yet with a direct implication that in order to bracket solutions one must keep track of the Schrödinger equation in both subspaces O and P. The variational principle in its conventional form yields upper bounds. This is a consequence of working in a certain subspace only. In perturbation theory, it is possible to give upper and lower bounds provided, as we shall see later, that we "keep track" of the orthogonal complement; if we neglect it we are left with approximations that do not bracket the energy. The truncations in Chapter III are an example of this situation.

In PTI Löwdin pointed out the connection of partitioning technique with iteration variation procedures in general, and with the Newton-Raphson method in particular. The following result is important.

Let $\mathcal{E}$ be an upper bound to the ground state energy, then $\mathcal{E}_1 \leq E_o \leq \mathcal{E}$. Clearly, from the variational principle:

$$E_o \leq \mathcal{E}^* = \frac{\langle \Psi_{\mathcal{E}} | H | \Psi_{\mathcal{E}} \rangle}{\langle \Psi_{\mathcal{E}} | \Psi_{\mathcal{E}} \rangle} \quad . \tag{1.17}$$

As in PTI, it is easy to see that

$$\mathcal{E}_1 \leq E_o \leq \mathcal{E}^*$$

Proof:

$$\mathcal{E}^* = \frac{\langle \psi | H | \psi_{\mathcal{E}} \rangle + \langle \phi_{\mathcal{E}} | H | \psi_{\mathcal{E}} \rangle}{1 + \langle \phi_{\mathcal{E}} | \phi_{\mathcal{E}} \rangle} = \frac{\mathcal{E}_1 + \mathcal{E} \langle \phi_{\mathcal{E}} | \phi_{\mathcal{E}} \rangle}{1 + \langle \phi_{\mathcal{E}} | \phi_{\mathcal{E}} \rangle}$$

$$= \mathcal{E} - \frac{\mathcal{E} - \mathcal{E}_1}{1 + \langle \phi_{\mathcal{E}} | \phi_{\mathcal{E}} \rangle} \leq \mathcal{E} \quad . \qquad \text{Q.E.D.}$$

The practical application of these results depends on the possibility of evaluating $\mathcal{E}_1$ and $\langle \phi_{\mathcal{E}} | \phi_{\mathcal{E}} \rangle$. We can't do it exactly, but it is possible to obtain approximations that preserve the inequalities. Instead of computing $\mathcal{E}_1$, it is possible to evaluate $\mathcal{E}_1' \leq \mathcal{E}_1$, which still brackets E if $E \leq \mathcal{E}$.

We should like to point out the following theorem:

Theorem 1.1:

If $\mathcal{E}_1' \leq \mathcal{E}_1 \leq E_o \leq \mathcal{E}^* \leq \mathcal{E} \leq \overline{E}_1$, where $\overline{E}_1$ is the first eigenvalue of PHP, $g(\mathcal{E}) = -\langle \phi_{\mathcal{E}} | \phi_{\mathcal{E}} \rangle$ satisfies the relations:

$$g(\mathcal{E}_1') \leq g(\mathcal{E}_1) \leq g(E_o) \leq g(\mathcal{E}^*) \leq g(\mathcal{E}). \tag{1.18}$$

The proof is very simple; it relies on the fact that $g(\mathcal{E}) = -f'(\mathcal{E})$ is a monotonous function for $-\infty < \mathcal{E} < \overline{E}_1$; $\lim_{\mathcal{E} \to -\infty} g(\mathcal{E}) = 0$; $\lim_{\mathcal{E} \to \overline{E}_1} g(\mathcal{E}) = \infty$. Further $g(\mathcal{E})$ is non decreasing; hence; $g(\mathcal{E}_A) \leq g(\mathcal{E}_B)$ for $\mathcal{E}_A \leq \mathcal{E}_B$, and this completes the proof.

Neither $g(\mathcal{E}_1)$ nor $g(E_o)$ are easily available. Equation (1.18) provides bounds in terms of $\mathcal{E}_1'$ and $\mathcal{E}$ which are known. The problem

of evaluating $g(\mathcal{E})$ itself will be discussed later. A generalization of Theorem 1.1 will be given in Chapter V.

The precision of the bracketing is determined by Eq. (1.15). If $|f'(E+\Theta\mathcal{E})| < 1$ the lower bound is going to be better than the upper bound, or in virtue of Eq. (1.18), if $g(\mathcal{E}) < 1$. In terms of Eq. (1.9) and Eq. (1.10) this means that if the reference function Ψ contributes more than 50 per cent towards the trial wave function $\Psi_{\mathcal{E}}$, the lower bound is better than the upper bound.

To conclude the general remarks on partitioning it should be pointed out that if the reference function Ψ is orthogonal to a particular Ψ_n, the associated eigenvalue, E_n, is not bracketed at all, thus yielding the only restriction on Ψ. The sharpness of the bracketing depends only on the propinquity of Ψ to Ψ_n.

1.2. Full and Reduced Resolvents Weinstein Functions

Given the Hamiltonian H, and the eigenvalue problem Eq. (1.1), there is a "resolution of the identity" and a spectral resolution of H in terms of the eigenoperators O_k:

$$\begin{aligned} HO_k &= E_k O_k \\ 1 &= \sum_k O_k \\ H &= \sum_k E_k O_k \quad . \end{aligned} \tag{1.19}$$

The operators O_k are self-adjoint and idempotent. Furthermore the

resolutions in Eq. (1.19) imply not only a sum over the discrete states, but the Stieltjes integral over the continuum spectrum. The conditions under which Eq. (1.19) hold, and their proofs can be found in von Neumann[14], Riesz, Nagy[15], and Lengyel[16]. For our present purposes, it is sufficient to assume that Eq. (1.19) holds for H and H_o, both self-adjoint operators.

Functions of operators may be defined in terms of their spectral resolutions and we have then:

$$f(H) = \sum_k f(E_k)\Theta_k \tag{1.20}$$

$$(\mathcal{E} - H)^{-1} = \sum_k (\mathcal{E} - E_k)^{-1} O_k \quad .$$

The coefficient of O_k blows up for $\mathcal{E} \to E_k$. The significance of this follows from considering

$$X = (\mathcal{E} - H)^{-1}\psi \tag{1.21}$$

for a given ψ.

$$\lim_{\mathcal{E}\to E_n} \frac{X}{\langle\psi|X\rangle} = \frac{\Psi_n}{\langle\psi|\Psi_n\rangle} \quad . \tag{1.22}$$

The connection between the full resolvent and the reduced resolvent was pointed out by Löwdin in PTX. It arises from the inhomogeneous equation (1.11):

$$(H - \mathcal{E})\Psi_{\mathcal{E}} = (\mathcal{E}_1 - \mathcal{E})\psi \quad .$$

Therefore:

$$\Psi_{\mathcal{E}} = (\mathcal{E}_1 - \mathcal{E})(H - \mathcal{E})^{-1}\psi = (\mathcal{E} - \mathcal{E}_1)X \quad . \tag{1.23}$$

The intermediate normalization implies:

$$1 = (\mathcal{E} - \mathcal{E}_1) \langle \psi | X \rangle$$

and then

$$\Psi_{\mathcal{E}} = \frac{X}{\langle \psi | X \rangle} = \frac{(\mathcal{E} - H)^{-1} \psi}{\langle \psi | (H - \mathcal{E})^{-1} | \psi \rangle} \tag{1.24}$$

$$\mathcal{E}_1 = \mathcal{E} - \langle \psi | X \rangle^{-1} = \mathcal{E} - \frac{1}{\langle \psi | (\mathcal{E} - H)^{-1} | \psi \rangle} \cdot \tag{1.25}$$

The full resolvent equations (1.24) and (1.25) are associated with the inhomogeneous equation (1.21). The inhomogeneous equation approach has been very successful. For a review of its applications see [6]. It was used in connection with perturbation theory. Within the same context we shall make appeal to it, but to solve equations to all orders, instead of a specific order of the perturbation series. This will be done in Chapters III and V.

The expression $\langle \psi | X \rangle$ is called the Weinstein function:

$$W(\mathcal{E}) = \langle \psi | (\mathcal{E} - H)^{-1} | \psi \rangle \cdot \tag{1.26}$$

Weinstein functions, and in general Weinstein determinants, have been introduced in the theory of "intermediate problems" by Weinstein[3]. The book by Gould[17] gives an account of its properties. In Appendix B of PTX, Löwdin discusses its relation to variations subject to a constraint. We should expect a connection with the eigenvalues of PHP as being determined by constrained variations. We shall require some use of the properties of PHP and T, therefore it is convenient to study W in some detail.

$W(\lambda)$ is monotonously decreasing:

$$W'(\mathcal{E}) = -\langle \psi | (\mathcal{E} - H)^{-2} | \psi \rangle < 0 \quad . \tag{1.27}$$

It has vertical asymptotes for $\mathcal{E} = E_k$, the eigenvalues of H. This can be seen by expanding the reference function ψ in terms of the eigenfunctions to H, thus obtaining:

$$W(\mathcal{E}) = \sum_{k=0}^{\infty} \frac{|a_k|^2}{\mathcal{E} - E_k} \tag{1.28}$$

with $a_k = \langle \Psi_k | \psi \rangle$.

What are the zeroes of $W(\mathcal{E})$? Consider the eigenvalue problem of $\bar{H} = PHP$.

$$\bar{H}\bar{\Psi} = \bar{E}\bar{\Psi} \quad .$$

As $P\bar{\Psi} = \bar{\Psi}$

$$P(H - \bar{E})\bar{\Psi} = 0$$

$$(H - \bar{E})\bar{\Psi} = \psi\langle\psi|H - \bar{E}|\bar{\Psi}\rangle = \psi\langle\psi|H|\bar{\Psi}\rangle$$

$$\bar{\Psi} = (H - \bar{E})^{-1}\psi\langle\psi|H|\bar{\Psi}\rangle \quad .$$

Finally, from the orthogonality between ψ and $\bar{\Psi}$:

$$0 = W(\bar{E})\langle\psi|H|\bar{\Psi}\rangle \quad .$$

Now, if

$$\langle\psi|H|\bar{\Psi}\rangle \neq 0,$$

$$W(\bar{E}) = 0 \ .$$

Therefore, the Weinstein function vanishes for those eigenvalues of PHP which are not simultaneously eigenvalues of H. The zeroes of $W(\mathcal{E})$ are the $\bar{E}_i$. (See Fig. 3.)

For $\mathcal{E} < E_{p+1}$, the following simple estimates of $W(\mathcal{E})$ are valid:

$$\sum_{k=0}^{p} \frac{|a_k|^2}{\mathcal{E}-E_k} > W(\mathcal{E}) > \sum_{k=0}^{p} \frac{|a_k|^2}{\mathcal{E}-E_k} + \frac{1 - \sum_{k=0}^{p} |a_k|^2}{\mathcal{E} - E_{p+1}} \quad . \qquad (1.29)$$

We have come this far in discussing the Weinstein function and found that its zeroes are the eigenvalues of PHP. This effort becomes meaningful when we consider the spectral resolution of T:

A starting point is Eq. (1.7):

$$P(\mathcal{E} - H)T = P \qquad (1.7)$$

or simply

$$(\mathcal{E} - \bar{H})T = P$$

$$T = (\mathcal{E} - \bar{H})^{-1}P = \sum_{k} (\mathcal{E} - \bar{E}_k)^{-1}\bar{O}_k P \quad .$$

Now in the subspace P, the resolution of the identity is replaced by

$$P = \sum_{k=1} \bar{O}_k ; \quad \bar{O}_k P = P\bar{O}_k = \bar{O}_k$$

where $\bar{O}_k = |\bar{\Psi}_k\rangle\langle\bar{\Psi}_k|$ is the projection operator associated with the k^{th} eigenfunction to $\bar{H}$.

We obtain then the spectral resolution:

$$T = \sum_{k=1} \frac{\bar{O}_k}{\mathcal{E} - \bar{E}_k} = \sum_{k=1} \frac{|\bar{\Psi}_k\rangle\langle\bar{\Psi}_k|}{\mathcal{E} - \bar{E}_k} \quad .$$

Finally, if $\mathcal{E} < \bar{E}_{p+1}$ the bounds

$$\sum_{k=1}^{p} \frac{\bar{O}_k}{\mathcal{E} - \bar{E}_k} \geq T \geq \sum_{k=1}^{p} \frac{\bar{O}_k}{\mathcal{E} - E_k} + \frac{P - \sum_{k=1}^{p} \bar{O}_k}{\mathcal{E} - E_{p+1}} \equiv T(p) \qquad (1.30)$$

hold, and are similar to the bounds in Eq. (1.29) for $W(\mathcal{E})$. In fact, spectral resolutions and bounds for the operator $T_o = \frac{P}{\mathcal{E} - H_o}$, defined in a similar way, are of analogous nature. One has to replace H by H_o, Ψ_n by Ψ_n^o, E_n by E_n^o, and of course $H_o\Psi_n^o = E_n^o\Psi_n^o$ must be satisfied.

It should be pointed out that there is another expression for the reduced resolvent T, in terms of the Weinstein function and the eigenvalues of H, given by Löwdin in Appendix A of PTXI. We give it here to illustrate a further relation between the E_i's and the $\bar{E}_k$'s through $W(\mathcal{E})$. The starting point is again Eq. (1.7):

$$P(\mathcal{E} - H)T = P \qquad . \qquad (1.7)$$

According to Eq. (1.3):

$$(\mathcal{E} - H)T + |\psi\rangle\langle\psi|HT = 1 - |\psi\rangle\langle\psi|$$

and

$$T = (\mathcal{E} - H)^{-1} - (\mathcal{E} - H)^{-1}|\psi\rangle\langle\psi| - (\mathcal{E} - H)^{-1}|\psi\rangle\langle\psi| HT \qquad . \qquad (1.31)$$

If we multiply by $\langle\psi|$:

$$0 = \langle\psi|(\mathcal{E} - H)^{-1} - W(\mathcal{E})\langle\psi| - W(\mathcal{E})\langle\psi|HT$$

which means

$$\langle\psi|HT = W(\mathcal{E})^{-1}\langle\psi|(\mathcal{E} - H)^{-1} - \langle\psi| \qquad .$$

Replacing in Eq. (1.31):

$$T = (\mathcal{E} - H)^{-1} - (\mathcal{E} - H)^{-1}|\psi\rangle\langle\psi| - [W(\mathcal{E})]^{-1}(\mathcal{E} - H)^{-1}|\psi\rangle\langle\psi|(\mathcal{E} - H)^{-1} + (\mathcal{E} - H)^{-1}|\psi\rangle\langle\psi| \quad .$$

Therefore,

$$T = (\mathcal{E} - H)^{-1} - \frac{(\mathcal{E} - H)^{-1}\, O\, (\mathcal{E} - H)^{-1}}{W(\mathcal{E})} \quad . \tag{1.32}$$

The spectral resolution of T in terms of the eigenfunctions of H is particularly interesting. For $\psi = \sum a_k \Psi_k$, we have:

$$W(\mathcal{E})(\mathcal{E} - H)^{-1} - (\mathcal{E} - H)^{-1}\, O\, (\mathcal{E} - H)^{-1}$$

$$= \sum_k \frac{a_k{}^2}{\mathcal{E} - E_k} \sum_e \frac{O_e}{\mathcal{E} - E_e} - \sum_{k,e} \frac{O_k O_e}{(\mathcal{E} - E_k)(\mathcal{E} - E_e)}$$

$$= \sum_k \sum_e \frac{a_k{}^2 O_e - O_k O_e}{(\mathcal{E} - E_k)(\mathcal{E} - E_e)} = \frac{1}{2} \sum_k \sum_e \frac{a_k{}^2 O_e + a_e{}^2 O_k - O_k O_e - O_e O_k}{(\mathcal{E} - E_k)(\mathcal{E} - E_e)}$$

$$= \frac{1}{2} \sum_k \sum_e \frac{\Omega_{ke}^{+} \Omega_{ke}}{(\mathcal{E} - E_k)(\mathcal{E} - E_e)}$$

where the operators Ω_{ke} are defined as:

$$\Omega_{ke} = a_e|\Psi_k\rangle - a_k|\Psi_e\rangle = -\Omega_{ek} \quad . \tag{1.33}$$

$$(\Omega_{ke}^{+}\Omega_{ke})^2 = \Omega_{ke}^{+}\Omega_{ke}\Omega_{ke}^{+}\Omega_{ke}$$

$$= \Omega_{ke}^{+}\Omega_{ke}(|a_k|^2 + |a_e|^2) \quad . \tag{1.34}$$

The $\Omega^{+}_{ke}\Omega_{ke}$ are, except for a constant factor, projectors and satisfy the important relation:

$$P = \frac{1}{2}\sum_{k}\sum_{e}\Omega^{+}_{ke}\Omega_{ke} \quad . \tag{1.35}$$

The reduced resolvent T can be written as:

$$T = W(\mathcal{E})^{-1}\frac{1}{2}\sum_{k}\sum_{e}\frac{\Omega^{+}_{ke}\Omega_{ke}}{(\mathcal{E}-E_k)(\mathcal{E}-E_e)} \tag{1.36}$$

which should be compared with Eq. (1.29). A similar expression should hold for T_o, in terms of E^o_e, Ψ^o_e and the analogous Ω^o_{ke} .

1.3. Wave and Reaction Operators

These concepts arise from the splitting of the Hamiltonian H into an unperturbed part H_o and a perturbation V: $H = H_o + V$, where V is by no means necessarily small. Let ψ_o be an eigenfunction to H_o corresponding to the eigenvalue E_o. Then the Schroedinger equation (1.1) may be transformed, using intermediate normalization ($\langle\psi_o|\Psi\rangle = 1$):

$$(H_o+V)\Psi = E\Psi \tag{1.37}$$

$$E_o + \langle\psi_o|V\,\Psi\rangle = E \quad . \tag{1.38}$$

If we define an operator W, the wave operator, by

$$W\psi_o = \Psi \tag{1.39}$$

and another operator t, the reaction operator, by $VW = t$ we have,

$$E = E_o + \langle\psi_o|VW|\psi_o\rangle = E_o + \langle\psi_o|t|\psi_o\rangle \quad . \tag{1.40}$$

These operators have been extensively studied by many authors in connection with bound and scattering states, stationary and time dependent problems. See reference [18] and the book by Kumar [19] which contains abundant references to the original papers. In PTIV and PTV they were discussed in connection with infinite order perturbation theory and exact selfconsistent fields, as well as in the derivation of the Rayleigh-Schrödinger and Brillouin-Wigner perturbation series. The freedom obtained by letting $\mathcal{E}$ become a variable at our disposal allowed, in PTIX, the evaluation of upper bounds of energy values in Rayleigh-Schrödinger perturbation theory, and in PTX and PTXI, lower bounds to the energy of ground and excited states. There are several possible extensions of Eqs. (1.39) and (1.40); one may have an arbitrary reference function; it may be a finite linear combination of eigenfunctions to H_o, or not expressible as a finite linear combination of eigenfunctions to H_o. Finally, one may have a reference space, spanned by a set of such functions.

Consider, for the time being, a single reference function. Define T and T_o as in Eq. (1.4), and the wave and reaction operator as follows:

$$W = 1 + TV \tag{1.41}$$

$$t = VW = V + VTV \quad . \tag{1.42}$$

If we use the fundamental identity, key to many relations in the theory $(A-B)^{-1} = A^{-1} + A^{-1}B(A-B)^{-1}$, we obtain

$$T = T_o + T_o VT = T_o(1+VT) \tag{1.43a}$$

$$TV = T_o t \tag{1.43b}$$

$$T = T_o + T_o tT_o \tag{1.43c}$$

and for the reaction operator:

$$t = V + VT_o t \tag{1.44a}$$

which may be written:

$$t = (1-VT_o)^{-1}V = V(1-T_o V)^{-1} \quad . \tag{1.44b}$$

Finally, for the wave operator we have:

$$W = (1-T_o V)^{-1} \quad . \tag{1.45}$$

Equation (1.43) is the Lippmann-Schwinger equation[20] derived in this way by K. Ohno[21]. If V has an inverse, we obtain

$$t = (V^{-1}-T_o)^{-1} \tag{1.46a}$$

or simply:

$$t^{-1} = V^{-1}-T_o \quad . \tag{1.46b}$$

Equations (1.45) and (1.46) will be the starting point of our discussion in Chapters III and V. Quite clearly the evaluation of Eqs. (1.45) and (1.46) implies solving the Schrödinger equation through Eq. (1.39) and Eq. (1.40). Actually, we need expressions that replace Eqs. (1.39) and (1.40) when the reference function is arbitrary and not a single eigenfunction to H_o. Multidimension partitioning techniques and the need to improve convergence through Eq. (1.15) establish the need of such an extension.

The starting point is the trial wave function $\Psi_{\mathcal{E}}$, as defined in Eq. (1.9):

$$\Psi_{\mathcal{E}} = \psi + TH\psi = (1+TH)\psi \tag{1.9}$$

$$= [1+(1-T_oV)^{-1}T_oH]\psi$$

$$= (1-T_oV)^{-1}[1 - T_oV+T_oH]\psi$$

$$\Psi_e = W(1+T_oH_o)\psi \tag{1.47}$$

Löwdin defined a <u>modified reference function</u> $\bar{\psi}$ by:

$$\bar{\psi} = (1+T_oH_o)\psi \ .$$

It is clear that if the reference function ψ is a linear combination of eigenfunctions to H_o, $\bar{\psi}$ and ψ are spanned by the same space. In general, we have

$$\Psi_{\mathcal{E}} = W\bar{\psi} \tag{1.48}$$

which contains Eq. (1.39) as a very special case, namely, $\psi = \psi_o$ and $\mathcal{E}_1 = \mathcal{E} = E$. We need an expression for $\mathcal{E}_1$. Hence, we consider

$$H + HTH = H_o + V + H_oTH_o + H_oTV + VTH_o + VTV$$

$$= H_o + t + H_o(T_o+T_otT_o)H_o + H_oT_ot + tT_oH_o$$

$$= H_o(1+T_oH_o) + (1+H_oT_o)t(1+T_oH_o) \ . \tag{1.49}$$

The bracketing function becomes now

$$\mathcal{E}_1 = \langle\psi|H_o|\bar{\psi}\rangle + \langle\bar{\psi}|t|\bar{\psi}\rangle \tag{1.50}$$

which, again, contains Eq. (1.38) as a very special case.

We conclude by stating that $\bar{\psi}$ is not normalized to unity, as ψ:

$$\langle\bar{\psi}|\bar{\psi}\rangle = 1 + \langle\psi|H_o T_o {}^2H_o|\psi\rangle \tag{1.51}$$

and that $\bar{\psi}$ depends on the energy variable $\mathcal{E}$.

Equation (1.50) is very general and has been the starting point of several applications[13]. The applicability depends on evaluating it exactly, or on obtaining a lower bound to it, $\mathcal{E}_1' \leq \mathcal{E}_1$, for the case when $\mathcal{E}$ is an upper bound to an eigenvalue E. The basis for this is discussed in the next section.

1.4. Operator Inequalities

An operator A is said to be greater or equal than B, if for all functions belonging to the intersection of the domains of A and B, the expectation values of A are larger or equal than those of B, that is;

Definition 1.1: $A \geq B$ iff for all $f \in D_A \cap D_B$, $\langle f|A|f\rangle \geq \langle f|B|f\rangle$

where D_A denotes the domain of A.

An operator is positive definite, $A > 0$, iff $\langle f|A|f\rangle > 0$.

An operator is non-negative definite, $A \geq 0$, iff $\langle f|A|f\rangle \geq 0$.

For a finite matrix, a necessary and sufficient condition for positive definiteness is that all the determinants

$$|A_k| = a_{ij}\,, \quad i,j = 1,2,\ldots,k; \quad k = 1,2,\ldots,n$$

must be positive. A necessary condition is that the determinant $|A| > 0$, and in general, an hermitian positive definite operator must necessarily have positive eigenvalues.

Theorem 1.2: (Ordering theorem)

If $A \leq B$, the eigenvalues to A, a_k, and the eigenvalues to B, b_k, satisfy $a_k \leq b_k$, in order. The proof is simple and resorts to the variation principle:

$$Au_k = a_k u_k; \quad Bv_k = b_k v_k, \quad k = 1,2,\ldots$$

$$a_1 \leq \langle v_1|A|v_1\rangle \leq \langle v_1|B|v_1\rangle = b_1 \quad .$$

For the first excited state, one repeats the reasoning but using a trial function $\psi = \alpha_1 v_1 + \alpha_2 v_2$, orthogonal to u_1, that is $\langle\psi|\psi\rangle = 1$; $\langle\psi|u_1\rangle = 0$. Then:

$$a_2 \leq \langle\psi|A|\psi\rangle \leq \langle\psi|B|\psi\rangle = |\alpha_1|^2 b_1 + |\alpha_2|^2 b_2 \leq b_2 \quad .$$

The inequality $a_3 \leq b_3$ follows from taking ψ as $\psi = \sum_{i=1}^{3} \alpha_i u_i$, normalized and orthogonal to u_1 and u_2. This process can be continued for higher eigenvalues. The converse of the theorem is not true. If $a_k \leq b_k$, it does not follow that $A \leq B$.

Theorem 1.3:

If $A > B$, it follows that $\Omega^+ A \Omega > \Omega^+ B \Omega$ for $\Omega f \in D_A \cap D_B$.

$$\langle f|A|f\rangle > \langle f|B|f\rangle \ ; \text{ take } f = \Omega g, \text{ then}$$

$$\langle g|\Omega^+ A \Omega|g\rangle > \langle g|\Omega^+ B \Omega|g\rangle \quad . \quad \text{Q.E.D.}$$

Inequalities of this type were discussed by Rellich[22] and Heinz[23].

Kato[24] discusses slightly different inequalities for linear operators, which are useful in the present context. These inequalities, in the sense of Kato, will be denoted by $\ll$ instead of $<$. Let S and T be linear operators.

Definition 1.2: $S \ll T$ if $D_S \supseteq D_T$ and $\|Sx\| \leq \|Tx\|$ for all $x \in D_T$.

If S and T are self-adjoint, $S \ll T$ is equivalent to $S^2 < T^2$ in the sense of Rellich. Kato proves the following two theorems for A and B self-adjoint:

Theorem 1.4.:

If $A \ll B$ and A^{-1} exists, it follows that B^{-1} exists and $B^{-1} \ll A^{-1}$.

Theorem 1.5. Let $A \geq 0$, $B \geq 0$, $A \gg B$. Then $A^{\nu} \gg B^{\nu}$ for $0 \leq \nu \leq 1$.

The concept of positive definite operators will prove to be very important in what follows. We may qualify somehow definition (1.1) by introducing the concept of domain of positivity R, associated with a given operator A. We say that $f,g \in R$ if this implies that $\langle f, Ag \rangle \geq 0$. This was discussed by Koecher[25]. The significance of this will become apparent when considering inner projections and expectation values of t for V positive definite.

Inequalities for inverses of operators appear to be useful. If $A \geq B > 0$, it follows that A^{-1} and B^{-1} exist, moreover we have:

Theorem 1.6.

If $A \geq B > 0$, it follows that $0 < A^{-1} \leq B^{-1}$. In PTX there is a simple proof of this theorem based on the identity

$$(A-B)^{-1} \equiv A^{-1} + A^{-1}BA^{-1} + A^{-1}B(A-B)^{-1}BA^{-1} \tag{1.52}$$

which can be used in the following way:

$$B^{-1} \equiv [A - (A-B)]^{-1} = A^{-1} + A^{-1}(A-B)A^{-1} + A^{-1}(A-B)B^{-1}(A-B)A^{-1}.$$

If $A-B > 0$, $A^{-1}(A-B)A^{-1} > 0$ by Theorem 1.3. Similarly as $B^{-1} > 0$, $A^{-1}(A-B)B^{-1}(A-B)A^{-1} > 0$. But then the theorem follows: $B^{-1} > A^{-1}$.

Theorem 1.6 states an order relation between A^{-1} and B^{-1} starting from an order relation for A and B. The question arises on order relations for f(A) and f(B), where f(A) is an arbitrary function of the operator A.

Loewner[26] studied the problem of what are the functions f(z) such that $A \geq B$ implies $f(A) \geq f(B)$. It turns out that these functions, called positive real functions, are generated by two simple functions; $cz + c_2$, where $c_1 > 0$ and $-z^{-1}$. The second one corresponds to Theorem 1.7.

Lengyel[27] showed that if $[A,B] = 0$ and A,B are positive, it follows that AB itself is positive. This proof is very general, and does not invoke the spectral resolutions of the operators. Let's assume that A and B are positive, self-adjoint permutable operators. Therefore we can choose a complete set of simultaneous eigenfunctions to A and B. Then expanding an arbitrary function in terms of this set we have:

$$\langle f|AB|f\rangle = \sum_{k,e} c_k^* c_e \langle u_k|AB|u_e\rangle$$

$$= \sum_{k,e} c_k^* c_e a_k b_e \delta_{ke} = \sum_k c_k{}^2 a_k b_k \geq 0 .$$

Thus we proved:

Theorem 1.7:

If $A \geq 0$, $B \geq 0$, $A = A^+$, $B = B^+$, $[A,B] = 0$, if follows that $AB \geq 0$.

We used the fact that a positive operator has non-negative eigenvalues. Lengyel's proof is more general than this one.

We are now in a position to examine the question: if $A \geq B$, under what conditions $A^2 \geq B^2$? Clearly z^2 is not a monotone matrix function, yet we can state that a sufficient condition for $A^2 \geq B^2$, if $A \geq B$ is that $[A,B] = 0$.

If $[A,B] = 0$, $(A-B)(A+B) \geq 0$ by Theorem 1.8. Then $(A-B)(A+B) = A^2 - B^2 \quad 0$.

Corollary: If $A \geq B$, $[A,B] = 0$, then $A^2 \geq B^2$.

Definition 1.3: Let $Q = Q^2 = Q^+$, $\bar{A} = QAQ$ is called the outer projection of A, where A is self-adjoint, bounded from below. Clearly, all functions in the orthogonal complement to Q, are eigenfunctions to $\bar{A}$ associated with the eigenvalue zero.

Theorem 1.8:

There is an order relation between the eigenvalues of A and those of $\bar{A}$, namely that, $a_k < \bar{a}_k$ in order, where $Au_k = a_k u_k$, and $\bar{A}\bar{u}_k = \bar{a}_k \bar{u}_k$. This is proven by Löwdin in PTX. The proof is simple and uses the variational principle:

$$a_1 \leq \langle \bar{u}_1 | A | \bar{u}_1 \rangle = \langle \bar{u}_1 | QAQ | \bar{u}_1 \rangle = \bar{a}_1 \quad .$$

For the first excited state consider a normalized variational function, orthogonal to u_1, which is simply a linear combination of $\bar{u}_1$ and $\bar{u}_2$. As in the proof of Theorem 1.2, it follows that $a_2 \leq \bar{a}_2$ and we obtain $a_3 \leq \bar{a}_3$, etc. Q is entirely arbitrary. In particular it may be the projection operator associated with a linear manifold $\mathfrak{F} = (f_1, f_2, \ldots, f_n)$

where the $\{f_n\}$ are linearly independent functions. Then

$$Q = |\mathfrak{f}\rangle \Delta^{-1} \langle \mathfrak{f}| = \sum_{k,e} |f_k\rangle (\Delta^{-1})_{ke} \langle f_e| \tag{1.53}$$

where

$$\Delta_{ke} = \langle \mathfrak{f} \mid \mathfrak{f} \rangle_{ke} = \langle f_k | f_e \rangle \ .$$

In Appendix A of PTX, Löwdin discusses these projection operators. Furthermore, he pointed out that for an orthonormal basis, $\mathfrak{F} = (\phi_1, \phi_2, \ldots, \phi_n)$, the operator QAQ is represented by a matrix having the elements $A_{ke} = \langle \phi_k | A | \phi_e \rangle$. Theorem 1.8 then asserts that the eigenvalues of this matrix are upper bounds to the eigenvalues of A, and further, that these bounds improve when the set $\mathfrak{F}$ is enlarged. This is a new proof of the Hylleraas and Undheim[28] and McDonald[29] result which actually goes beyond Theorem 1.8 because it states that the eigenvalues of approximation k (k-dimensional matrix) are separated by those of approximation k - 1. Perhaps it should be pointed out that this theorem is originally due to Cauchy[30] and Poincaré[31]. A discussion of the accuracy of the variational approximations to the excited states is left for Chapter II.

Definition 1.4: If A is a positive definite self-adjoint operator, we define its inner projection A' by $A' = A^{\frac{1}{2}} Q A^{\frac{1}{2}}$, where Q is an arbitrary projection operator.

Note that if A is a multiplicative operator, its square root is simply the square root of the function characterizing the operator. If A is a general differential operator, the square root may be defined in

terms of the spectral resolution $A = \sum a_k |u_k\rangle\langle u_k|$, where $a_k > 0$, then $A^{\frac{1}{2}} = \sum a_k^{\frac{1}{2}} |u_k\rangle\langle u_k|$ is the "positive square root."

The inner projection may be defined for a non-positive definite operator, but only in its domain of positivity R. For instance, let O be the projection operator associated with the subspace R. Then $OAO > 0$, and A has a positive square root. The important property of inner projections is:

Theorem 1.9:

If A' is an inner projection of A, then $0 < a' < a$. As both Q and 1 - Q are positive and bounded by 1, i.e.,

$$1 \geq \langle\psi|Q|\psi\rangle = \langle\psi|Q^2|\psi\rangle = \langle Q\psi|Q\psi\rangle \geq 0$$

$$\langle\psi|1-Q|\psi\rangle = 1 - \langle\psi|Q|\psi\rangle \geq 0$$

it follows, as a consequence of Theorem 1.3, that:

$$0 < \langle\psi|A'|\psi\rangle = \langle\psi|A^{\frac{1}{2}}QA^{\frac{1}{2}}|\psi\rangle < \langle\psi|A|\psi\rangle \quad . \tag{1.54}$$

Again Q is entirely at our disposal. One may define inner projections on linear manifolds. Löwdin introduced the inner projection concept in PTX. Specific choices of the projection yield formulas that have been used by some authors. Consider a linear manifold $\mathfrak{f}$, with metric $\Delta = \langle\mathfrak{f}|\mathfrak{f}\rangle$. Then, a generic inner projection is:

$$A' = A^{\frac{1}{2}}|\mathfrak{f}\rangle\Delta^{-1}\langle\mathfrak{f}|A^{\frac{1}{2}}, \quad \Delta = \langle\mathfrak{f}|\mathfrak{f}\rangle \quad . \tag{1.55}$$

By the transformation $A^{\frac{1}{2}}|\mathfrak{f}\rangle = |g\rangle$, we obtain

$$A' = A|g\rangle\Delta^{-1}\langle g|A, \quad \Delta = \langle g|A|g\rangle \quad , \tag{1.56}$$

the Aronszajn projection[32], of extended use[33].

The transformation $A^{\frac{1}{2}}|\mathfrak{k}\rangle \overset{\pi}{\to} |h\rangle$ yields the Bazley projection:

$$A' = |h\rangle\Delta^{-1}\langle h|, \quad \Delta = \langle h|A^{-1}|h\rangle \tag{1.57}$$

This form was successfully used by Bazley and Fox in pioneering work on lower bounds to the eigenvalues of the Schrödinger equation[34].

The application of the operator inequalities introduced in this section is of two types:

One may use Theorem 1.2, and have an order relation between the eigenvalues of A and B, $A \prec B$. This is the "leitmotiv" of the Weinstein-Aronszajn-Bazley-Fox methods. This implies counting the lower eigenvalues and assuring that no eigenvalue is lost in the construction of the "intermediate Hamiltonians" $H^{(k)}$, $H^{(k)} \preceq H$, with $E_n^{(k)} \leq E_n$, in order.

The alternative is to use the partitioning formula in Eq. (1.51), and compute lower bounds to $\langle\bar{\psi}|t|\bar{\psi}\rangle$. If $t > 0$ it is possible to construct an inner projection $t' \prec t$. But we don't actually need that $t > 0$; in fact, as we shall see, it is possible to construct lower bounds to $\mathcal{E}_1$ through inner projections of V, or truncations of T or T_o, or combinations of these, as it was discussed by Löwdin in PTX, and PTXI. We shall present some further comments on this and on the connection with the intermediate problems. Again, an inner projection of t can be constructed within its domain of positivity, the condition $t > 0$ being too strong.

CHAPTER II

ACCURACY OF EIGENVALUES AND EIGENFUNCTIONS

There has been considerable work on the accuracy of eigenvalues and eigenfunctions. For the former, upper and lower bounds are the natural estimates. Local deviations and norm deviations of the type in Eq. (1.16) are used for the wave functions. In this section, we shall discuss Temple-like formulae for lower bounds and Eckart-type criteria for accuracy of variational wave functions. The motivation is that Temple-like criteria, even though not fully ab initio, have been widely used and are extremely accurate. Approximate variational functions are used to compute all kinds of properties, for ground and excited states, and these depend heavily on the accuracy of the functions. The connection between Temple-like formulae and partitioning formulae will be established and the use of lower bounds for excited states in estimating the accuracy of excited variational wave functions will be emphasized.

2.1. Temple Formula

It was obtained by Temple [1], and discussed by Kato[35], Hylleraas[9], and Löwdin[36]. It requires the calculation of expectation values of H^2, which is a computational complication, and estimates of neighbouring eigenvalues, not necessarily available. This last requirement is not needed in the Weinstein[37] and Crawford[38] formulae, which we discuss briefly: let E_o be the ground state of

Eq. (1.1). Then the variational principle states, for a normalized trial function ψ.

$$E_o \leq \langle\psi|H|\psi\rangle = \langle H\rangle \quad . \tag{2.1}$$

If $\langle H\rangle < \frac{1}{2}(E_o+E_1)$, the following expression is positive:

$$J = \langle\psi|\left\{(H-\langle H\rangle)^2 - (E_o-\langle H\rangle)^2\right\}|\psi\rangle > 0 \quad . \tag{2.2}$$

This can be seen by expanding ψ in terms of the eigenfunctions to H, and using the property that H is self-adjoint:

$$J = \sum_{k=0} [(E_k-\langle H\rangle)^2 - (E_o-\langle H\rangle)^2]\, c_k^{\,2} > 0$$

where the c_k's are the coefficients in the expansion of ψ in terms of the Ψ_k's.

$$(H-\langle H\rangle)^2 > (E_o-\langle H\rangle)^2 \tag{2.3}$$

or

$$(\Delta H)^2 = \langle H^2\rangle - \langle H\rangle^2 > (E_o-\langle H\rangle)^2$$

which yields

$$E_o < \langle H\rangle - \Delta H \tag{2.4}$$

which is the Weinstein formula. In order to apply it, we must know that $\langle H\rangle$ is "good enough," in the sense that $\langle H\rangle < \frac{1}{2}(E_o+E_1)$.

Temple's formula is easily derived from the consideration of the operator $\Omega_{ij} \equiv (H-E_i)(H-E_j)$, where E_i and E_j are neighbouring eigenvalues, i.e., $i = j\pm1$. Ω and H have the same eigenfunctions, and the eigenvalues are $\omega_k = (E_k-E_i)(E_k-E_j) \geq 0$. Then $\Omega \geq 0$, and for a normalized trial function ψ:

$$0 \leq \langle\psi|\Omega_{ij}|\psi\rangle = \langle H^2\rangle - \langle H\rangle^2 + (\langle H\rangle - E_i)(\langle H\rangle - E_j) \ .$$

Let $\langle H\rangle$ be contained in the interval (E_i, E_j), then

$$(\langle H\rangle - E_i)(E_j - \langle H\rangle) \leq (\Delta H)^2$$

and let $j = i \pm 1$. This yields the inequalities:

$$\langle H\rangle - \frac{(\Delta H)^2}{E_{i+1} - \langle H\rangle} \leq E_i \leq \langle H\rangle + \frac{(\Delta H)^2}{\langle H\rangle - E_{i-1}} \ . \tag{2.5}$$

In particular, for the ground state, this reduces to:

$$E_o \geq \langle H\rangle - \frac{(\Delta H)^2}{E_1 - \langle H\rangle} \ . \tag{2.6}$$

the well-known Temple result. This formula has been used by several authors[39]. Knowledge of E_1, the first excited eigenvalue of the same symmetry is needed, or at least a lower bound to it. This limits its applicability, as well as a fully <u>a priori</u> calculation of the errors involved. Hylleraas[9] suggested improved formulæ but they involve higher powers of H, thus their usefulness is restricted. Wilson[40] gave a proof of Eq. (2.6) based on the intermediate problems. In PTIV Löwdin suggested that (2.6) should follow from the partitioning formula in Eq. (1.12). The connection has not been established explicitly before, and it is interesting in the sense that it allows comparison of the partitioning method for computing lower bounds which is an <u>a priori</u> method, with Eq. (2.6) which is an accurate, though a <u>non a priori</u> formula.

In order to derive Eq. (2.6) from Eq. (1.12), we need a bound for T: If $\xi < \bar{E}_1$, Eq. (1.3)) reduces to:

$$T \geq \frac{P}{\mathcal{E} - \overline{E}_1} \tag{2.7}$$

and theorem 1.3 implies that

$$HTH \geqslant \frac{HPH}{\mathcal{E} - \overline{E}_1} \quad . \tag{2.8}$$

Therefore for $E_o < \mathcal{E} < \overline{E}_1$, we have a lower bound to $\mathcal{E}_1$:

$$\mathcal{E}_1 = \langle\psi|H+HTH|\psi\rangle \geq \langle\psi|H+\frac{HPH}{\mathcal{E}-\overline{E}_1}|\psi\rangle = \mathcal{E}_1'$$

which means

$$E_o \geq \langle H\rangle - \frac{(\Delta H)^2}{\overline{E}_1 - \mathcal{E}} \quad . \tag{2.9}$$

This is already very similar to Temple's formula, and the best possible bound it can give is for $\mathcal{E} = E_o$. We do not know $\overline{E}_1$, but any lower bound to it will do, because the inequality is preserved if $E_o \leq \mathcal{E} \leq \overline{E}_1' \leq \overline{E}_1$. We shall present some lower bounds to $\overline{E}_1$ derived by Löwdin in PTX.

Consider Eq. (1.29) for $\mathcal{E} < E_1$, which reduces to:

$$\frac{|a_o|^2}{\mathcal{E} - E_o} > W(\mathcal{E}) > \frac{|a_o|^2}{\mathcal{E} - E_o} + \frac{1 - |a_o|^2}{\mathcal{E} - E_1} \tag{2.10}$$

where $a_i = \langle\Psi_i|\psi\rangle$.

As $W(\mathcal{E})$ has negative slope and its zeroes are the eigenvalues of PHP, the $\overline{E}_i$'s, we conclude that if we set the left hand side of Eq. (2.10) equal to zero we obtain an upper bound to $\overline{E}_1$, and if we set the right hand side equal to zero we obtain a lower bound to $\overline{E}_1$. Then the solution of

$$(\mathcal{E} - E_1)|a_o|^2 + (\mathcal{E} - E_o)(1 - |a_o|^2) = 0$$

is a lower bound to $\bar{E}_1$, that is

$$E_o(1 - |a_o|^2) + E_1|a_o|^2 < \bar{E}_1 \quad . \tag{2.11}$$

At this state, it is convenient to introduce Eckart's criterion[2] for the accuracy of an approximate wave function. In its operator form it states:

$$\frac{(H-E_o)}{E_1 - E_o} \geq 1 - |\Psi_o\rangle\langle\Psi_o| \quad . \tag{2.12}$$

The proof follows from considering the operator $H-E_o$:

$$H-E_o = \sum_{k\neq 0} (E_k-E_o)O_k \geq \sum_{k\neq 0} (E_1-E_o)O_k = (E_1-E_o)(1-O_o) \geq 0.$$

Applying Eq. (2.12) to ψ we obtain the familiar expression:

$$\frac{\langle H\rangle - E_o}{E_1 - E_o} \geq 1 - |a_o|^2 \quad . \tag{2.13}$$

Substitution into Eq. (2.11) yields:

$$\bar{E}_1 > E_1 + (E_o-E_1)(1-|a_o|^2) \geq E_1 + E_o - \langle H\rangle \; . \tag{2.14}$$

The question now is how to transform Eq. (2.9) into Eq. (2.6). We will show that there is a value of $\mathcal{E}$, compatible with the constraints $E_o \leq \mathcal{E} \leq \bar{E}_1$, that verifies

$$\bar{E}_1 - \mathcal{E} = E_1 - \langle H\rangle \quad . \tag{2.15}$$

According to Eq. (2.15):

$$\mathcal{E} = \bar{E}_1 + \langle H\rangle - E_1 < \bar{E}_1$$

if $\langle H\rangle < E_1$. Furthermore, Eq. (2.14) implies

$$\mathcal{E} > E_1 + E_o - \langle H\rangle + \langle H\rangle - E_1 = E_o \quad .$$

Therefore Eq. (2.15) is compatible with the constraints on $\mathcal{E}$, and Eq. (2.6) follows from Eq. (2.9). If we could have better lower bounds to $\bar{E}_1$ than Eq. (2.14), Eq. (2.9) could be used to bypass Temple's formula. In particular, bounds to $\bar{E}_1$ independent of E_o and E_1 will give a modification of Temple's formula that is a priori in the sense that it will not depend on E_1, and we will present those in Chapter V.

We have used Eq. (2.12), which is a simple form of Eckart's criterion. This shows that the problem of obtaining lower bounds to E_i and $\bar{E}_i$ is coupled to the determination of the coefficients a_i in $\psi = \Sigma a_i \Psi_i$. But this is an important problem per se: given a trial function for the i^{th} excited state, how close is it to Ψ_i? Before we may proceed, we should consider this problem:

2.2. Eckart-type Formulae

Our goal is to obtain bounds for $\|\Phi_k - \Psi_k\| = \int |\Phi_k - \Psi_k|^2 dv$ where $H\Psi_k = E_k\Psi_k$, and Φ_k is the k^{th} normalized eigenvector of a secular problem of order k. Furthermore, it will be interesting to have pointwise bounds, that is, bounds for $|\Phi_k(\vec{\tau}) - \Psi_k(\vec{\tau})|$.

There has been a considerable amount of work in this area. To consider but a few of the authors, we should mention Shull and Löwdin[41], Weinberger[42], and Lengyel[43] for norm bounds, and Diaz and Greenberg [44], Kinoshita[45], Synge[46], and Rédei[47] for point wise bounds.

The bounds presented by Löwdin and Shull are extensions of Eq. (2.13), which is a bound for $1 - |a_o|^2$ in terms of $\langle H \rangle - E_o$. Let us denote by J_k the k^{th} eigenvalue of the secular equation of order M.

Then

$$\langle \Phi_k | H | \Phi_e \rangle = J_k \delta_{ke}; \quad \langle \Phi_k | \Phi_e \rangle = \delta_{ke} \ . \tag{2.16}$$

What follows depends on the assumption that H is a self-adjoint operator bounded from below, with a partially discrete spectrum. Further, the results are valid for the discrete part of the spectrum only, below the continuum. The multiplicities of the eigenvalues must be taken into account.

Consider $J_k - E_k$, and expand Φ_k in terms of the complete set $\{\Psi_e\}$, $\Phi_k = \sum_{e=0}^{\infty} a_{ke} \Psi_e$:

$$J_k - E_k = \langle \Phi_k | H - E_k | \Phi_k \rangle = \sum_{e=0}^{\infty} (E_e - E_k) |a_{ek}|^2 \tag{2.17}$$

where

$$a_{ek} = \langle \Psi_e | \Phi_k \rangle; \quad \sum_{e=0}^{\infty} |a_{ek}|^2 = 1.$$

We may transform Eq. (2.17) into:

$$J_k - E_k = \sum_{e=0}^{k-1} (E_e - E_k) |a_{ek}|^2 + \sum_{e=k+1}^{\infty} (E_e - E_k) |a_{ek}|^2 .$$

$$\geq \sum_{e=0}^{k-1} (E_e - E_k) |a_{ek}|^2 + (E_{k+1} - E_k)\left(1 - \sum_{e=0}^{k-1} |a_{ek}|^2 - |a_{kk}|^2\right)$$

$$= - \sum_{e=0}^{k-1} (E_{k+1} - E_e) |a_{ek}|^2 + (E_{k+1} - E_k)(1 - |a_{kk}|^2) \ .$$

Therefore:

$$1 - |a_{kk}|^2 \leq \frac{J_k - E_k + \sum_{e=0}^{k-1} (E_{k+1} - E_e)|a_{ek}|^2}{E_{k+1} - E_k} \quad . \tag{2.18}$$

Löwdin and Shull point out that the problem is to estimate the $|a_{ek}|^2$ in terms of the $J_i - E_i$. We should note that the first term in the sum in the numerator is $(E_{k+1} - E_o)|a_{ok}|^2$. The nature of the spectra of quantum mechanical problems is such that the differences $E_{k+1} - E_o$ are rather large; on the other hand, if the approximation is reasonable, $|a_{ok}|^2$ should be small and the two effects cancel out. The approximations involved in estimating $|a_{ek}|^2$ may destroy this feature, as we will see now. Following Löwdin and Shull, we introduce an auxiliary function

$$\Phi = \sum_{\alpha=0}^{k} \phi_\alpha \mu_\alpha = \sum_{e=0}^{\infty} \psi_e d_e \tag{2.19}$$

with the restriction:

$$\sum_{\alpha}^{k} |\mu_\alpha|^2 = 1.$$

Clearly

$$d_e = \sum_{\alpha=0}^{k} a_{e\alpha} \mu_\alpha, \quad \sum_{e=0}^{\infty} |d_e|^2 = 1 \quad . \tag{2.20}$$

Let us choose the multipliers μ_α such that

$$d_o = d_1 = \ldots = d_{k-1} = 0. \tag{2.21}$$

Consider now:

$$\langle \textcircled{H} | H | \textcircled{H} \rangle = \sum_{\alpha=0}^{k} |\mu_\alpha|^2 J_\alpha = \sum_{e=0}^{\infty} |d_e|^2 E_e$$

$$\geq \sum_{e=k}^{\infty} |d_e|^2 E_e \geq E_k \sum_{e=k}^{\infty} |d_e|^2 > E_k$$

which may be rewritten:

$$\sum_{e=0}^{k-1} (J_e - E_k) |\mu_e|^2 \geq (E_k - J_k) |\mu_k|^2 \quad . \tag{2.22}$$

Assume that the approximation is so good that $J_o \leq J_1 \leq \ldots \leq J_{k-1} \leq E_k$, hence $E_k - J_e \geq 0$ for all $e < k$ and Eq. (2.22) implies:

$$\left| \frac{\mu_e}{\mu_k} \right|^2 \leq \frac{J_k - E_k}{E_k - J_e} \tag{2.23}$$

But Eq. (2.20) and Eq. (2.21) yield the following expression for A_{ek}:

$$a_{ek} = - \sum_{\alpha=0}^{k-1} a_{e\alpha} \frac{\mu_\alpha}{\mu_k} \tag{2.24}$$

hence,

$$|a_{ek}| \leq \sum_{\alpha=0}^{k-1} \left| \frac{\mu_\alpha}{\mu_k} \right| \leq \sum_{e=0}^{k-1} \left\{ \frac{J_k - E_k}{E_k - J_e} \right\}^{\frac{1}{2}} = (J_k - E_k)^{\frac{1}{2}} A \tag{2.25}$$

where

$$A = \sum_{e=0}^{k-1} (E_k - J_e)^{-\frac{1}{2}}$$

Replacing this in Eq. (2.18) we finally obtain the Löwdin-Shull formula:

$$1 - |a_{kk}|^2 \leq \frac{J_k - E_k}{E_{k+1} - E_k} \left\{ 1 + A^2 \sum_{e=0}^{k-1} (E_{k+1} - E_e) \right\} . \qquad (2.26)$$

If A^2 is small, which is the case when J_i is much closer to E_i than to E_{i+1}, the sum of the terms $(E_{k+1} - E_e)$ is multiplied by a small number, thus compensating the fact that $E_{k+1} - E_o$ is, in general, rather large in atomic and molecular spectra. We can say that Eq. (2.26) will give worse bounds with increasing k. By making use of spectral representations, Lengyel[43] derived a somewhat simpler formula, which is not a consequence of Eq. (2.26)

$$1 - |a_{kk}|^2 \leq \frac{J_k - E_k}{E_{k+1} - E_k} \left\{ 1 + \frac{E_{k+1} - E_o}{J_k - J_{k-1}} \right\} . \qquad (2.27)$$

The same considerations apply to Eq. (2.27): The fraction $(E_{k+1} - E_o)\ (J_k - J_{k-1})$ increases with k and can become very large even with small k, limiting the usefulness of Eq. (2.27), which is nevertheless slightly better than Eq. (2.26).

If we denote by E_i' a lower bound to E_i, Eq. (2.27) may be replaced by:

$$1 - |a_{kk}|^2 \leq \frac{J_k - E_k'}{J_{k+1} - E_k'} \left\{ 1 + \frac{J_{k+1} - E_o'}{J_k - J_{k-1}} \right\} \qquad (2.28)$$

which removes the dependence on the exact eigenvalues, by introducing the lower bounds to the ground state and the state under consideration.

The last equation shows that the problem of estimating the accuracy of excited state trial wave functions is coupled to the evaluation of lower bounds.

Lengyel also presented a bound for $1 - |a_{kk}|^2$ based on a successive determination of bounds for $1 - |a_{ee}|^2$, e=0,1,...,k, but its accuracy diminishes with increasing k. On the other hand, Eq. (2.27) and Eq. (2.28) are interesting applications of the spectral theorem to this problem. For completeness, we present a formula due to Weinberger[42] who made a careful estimate of the terms appearing in Eq. (2.18). In simplified form it reads:

$$1 - |a_{kk}|^2 \leq \frac{J_k - E'_k}{E'_{k+1} - E'_k} \left\{ 1 - \frac{(J_k - E'_k)(J_{k-1} - E'_o)}{(J_k - J_{k-1})(E'_k - E'_o)} \right\} + \frac{(J_k - E'_k)(J_{k-1} - E'_o)}{(J_k - J_{k-1})(E'_k - E'_o)} \quad . \tag{2.29}$$

Equation (2.29) has the advantage of having the factors $(J_{k-1} - E'_o)$ and $(E'_k - E'_o)$ explicitly as a ratio, thus there are no unduly large terms spoiling the bounds, and it reduces to Eckart's formula in the case of the ground state.

Formulae of the type in Eqs. (2.26) - (2.29) have not been used very extensively because we lack knowledge of accurate lower bounds E'_i, but should be kept in mind for future reference, because, through Eq. (1.27) they yield bounds for the Weinstein function. Furthermore, Eq. (2.13) as well as Eqs. (2.26) - (2.29) are of the type $|a_{kk}|^2 \geq b \geq 0$. It certainly is important to find, if at all possible bounds of the type $1 \geq c \geq |a_{kk}|^2$. Work in this direction was done by Rayner[44], which we will discuss in the future, in connection with properties other than energy. The estimates of the $|a_{kk}|^2$ will prove useful in applying formulae involving the Weinstein function, which connects the eigenvalues

of H with the eigenvalues of PHP, hence whenever reduced resolvents for arbitrary reference functions are employed.

2.3. A Numerical Appraisal of Eckart-type Formulae

Before going into quantum mechanical applications of Eq. (2.13) and Eq. (2.26) to Eq. (2.29), it is necessary to realize that they may give worse bounds than expected. Both the Eckart formula in Eq. (2.13) and the Temple formula give sharp bounds. By this we mean that they become equalities instead of inequalities under special circumstances, namely, that the trial function considered is a linear combination of the ground and the first excited states of H_o. But this event is very unlikely in general. It is important then, to compare the different formulae in a case where we know the exact solutions. For this purpose it is enough to consider a simple 3x3 matrix:

$$A = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 3 & 1 \\ 0 & 1 & 23 \end{pmatrix} . \tag{2.30}$$

The eigenvalues can be obtained by solving the characteristic equation or, most easily, by partitioning. They are:

$$\begin{aligned} \alpha_1 &= 0.579166 \\ \alpha_2 &= 3.370846 \\ \alpha_3 &= 23.049988 \end{aligned} \tag{2.31}$$

The first two eigenvectors are:

$$u_1 = \begin{pmatrix} 0.921570 \\ -0.387829 \\ 0.017276 \end{pmatrix} \quad . \tag{2.32}$$

$$u_2 = \begin{pmatrix} 0.388207 \\ 0.920378 \\ -0.046889 \end{pmatrix}$$

We shall consider a projection PAP with

$$P = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad . \tag{2.33}$$

This gives for $\bar{A}$:

$$\bar{A} = \begin{pmatrix} 1 & 1 \\ 1 & 3 \end{pmatrix} \quad , \tag{2.34}$$

with eigenvalues

$$\begin{aligned} \bar{\alpha}_1 &= 2 - \sqrt{2} = 0.585786 \\ \bar{\alpha}_2 &= 2 + \sqrt{2} = 3.414214 \end{aligned} \tag{2.35}$$

and eigenvectors:

$$\begin{aligned} \bar{u}_1 &= \begin{pmatrix} \frac{1}{2}(2+\sqrt{2})^{\frac{1}{2}} \\ -\frac{1}{2}(2-\sqrt{2})^{\frac{1}{2}} \end{pmatrix} = \begin{pmatrix} 0.923879 \\ -0.382683 \end{pmatrix} \\ \bar{u}_2 &= \begin{pmatrix} \frac{1}{2}(2-\sqrt{2})^{\frac{1}{2}} \\ \frac{1}{2}(2+\sqrt{2})^{\frac{1}{2}} \end{pmatrix} = \begin{pmatrix} 0.382683 \\ 0.923879 \end{pmatrix} \quad . \end{aligned} \tag{2.36}$$

We may test Temple's formula. For this we need A^2. A lower bound to a_1 is:

$$\alpha_1 > \alpha_1 - \frac{\langle \bar{u}_1 | A^2 | \bar{u}_1 \rangle - \langle \bar{u}_1 | A | \bar{u}_1 \rangle^2}{a_2 - \bar{a}_1} \tag{2.37}$$

as a trivial application of Eq. (2.6). This gives

$$\alpha_1 \geq 0.58786 - 0.052583 = 0.533203$$

which is not a very good lower bound and in fact is suggesting that we should not expect very good results from the Eckart criterion in this example.

We can now compute $\langle u_1 | \bar{u}_1 \rangle$ and $\langle u_2 | \bar{u}_2 \rangle$ exactly:

$$a_{11} = \langle u_1 | \bar{u}_1 \rangle = 0.999835; \quad a_{22} = \langle u_2 | \bar{u}_2 \rangle = 0.998878$$

which means then:

$$1 - \alpha_{11}^2 = 0.000331, \quad 1 - \alpha_{22}^2 = 0.00224 \quad . \tag{2.38}$$

Eckart's criterion, Eq. (2.13), applied to Eq. (2.30) gives:

$$1 - a_{11}^2 \leq \frac{\bar{\alpha}_1 - \alpha_1}{\alpha_2 - \alpha_1} = 0.00237 \quad . \tag{2.39}$$

The bounds for $1 - a_{22}^2$ are:

$$\begin{aligned} 1 - a_{22}^2 &\leq 0.0199 \text{ from Eq. (2.26)} \\ 1 - a_{22}^2 &\leq 0.0197 \text{ from Eq. (2.27)} \\ 1 - a_{22}^2 &\leq 0.00228 \text{ from Eq. (2.29).} \end{aligned} \tag{2.40}$$

We see that Eckart's criterion gives considerably more error than Temple's bound. We said before that both formula are sharp, and

this follows from considering $\psi = a_o\Psi_o + a_1\Psi_1$; $|a_o|^2 + |a_1|^2 = 1$. Then

$$\langle H\rangle = |a_o|^2E_o + |a_1|^2E_1 = E_1 + |a_o|^2(E_o-E_1)$$

or

$$|a_o|^2 = \frac{\langle H\rangle - E_1}{E_o - E_1}$$

which is Eckart's Eq. (2.13) when the equality holds. Similarly if we consider $(H-E_o)(H-E_1)$, its expectation value over ψ, is zero, i.e.:

$$(\Delta H)^2 + (\langle H\rangle - E_o)(\langle H\rangle - E_1) = 0$$

from which Temple formula follows as an equality.

The bounds for $1 - a_{22}^2$, from Eqs. (2.26) and (2.27) have, roughly, the same error as Temple's formula, but Weinberger's bound is very accurate. If this is true in practical application, it remains to be seen but at this time the existence of these formula suggests further work in connection with $W(\varepsilon)$.

CHAPTER III

PARTITIONING TECHNIQUE AND PERTURBATION THEORY

In PTIV and PTX, Löwdin discussed the various connections between partitioning technique and the Brillouin-Wigner (B-W) and Raileigh-Schrödinger (R-S) perturbation expansions. They stem out of Eq. (1.50) by using the relation in Eq. (1.52) for T. Löwdin discussed the derivation of the various expansions and some convergence criteria.

In this chapter we intend to show the connection with another expansion, the Feenberg perturbation series [5]. We present a derivation of the Feenberg series by using successive partitioning technique, and discuss some of its properties as well as methods of solution.

3.1. Brillouin-Wigner Perturbation Theory

If in Eq. (1.48) we let $\psi = \psi_o$, where ψ_o is an eigenfunction of H_o, and apply Eq. (1.52) we get a BW type series, namely,

$$\Psi_\mathcal{E} = \sum_{k=0}^{\infty} (T_o V)\psi_o = \psi_o + T_o V\psi_o + T_o V T_o V\psi_o + \ldots$$

$$= \psi_o \sum_{k=0}^{\infty} (T_o V)^k \psi_o \qquad . \tag{3.1}$$

$$\mathcal{E}_1 = E_o^o + \sum_{k=0}^{\infty} \langle \psi_o | V(T_o V)^k | \psi_o \rangle = E_o^o + \langle \psi_o | V | \psi_o \rangle$$

$$+ \langle \psi_o | V T_o V | \psi_o \rangle + \ldots = E_o + \langle \psi_o | V \sum_{k=0}^{\infty} (T_o V)^k | \psi_o \rangle \ . \tag{3.2}$$

This series, due to Brillouin[49] and Wigner[50] has been extensively discussed in the literature, where the interest has been focused in the points $\mathcal{E}_1 = \mathcal{E} = E$.

If we restrict ourselves to positive definite perturbations, $V > 0$, and consider values of $\mathcal{E} < E_1^o$, from Eq. (1.30) it follows that

$$T_o \leq \frac{\bar{0}_1}{\mathcal{E} - \bar{E}_1^o} = \frac{0_1}{\mathcal{E} - E_1^o} \leq 0 \tag{3.3}$$

hence $-T_o \geq 0$. From theorem 1.6, $V > 0$ implies $V^{-1} > 0$. Applying these results to Eq. (1.46):

$$t^{-1} = V^{-1} - T_o \geq V^{-1} > 0.$$

By theorem 1.7 again,

$$0 < t < V \ . \tag{3.4}$$

Therefore, the value of $\mathcal{E}_1$ is bracketed by:

$$E_o \leq E_o + \langle \psi_o | t | \psi_o \rangle = \mathcal{E}_1 \leq E_o + \langle \psi_o | V | \psi_o \rangle \ . \tag{3.5}$$

On the other hand, the series expansion may or may not converge. Examination of the terms appearing in Eq. (3.2) shows that the ones of even order are positive, and that those of odd order are negative. Therefore the series is alternating, and it will converge if and only if the magnitude of the n-th term goes to zero when n goes to infinity.

We can write this condition on the terms of Eq. (3.2) as a condition on the operator t, expressed in symmetric form:

$$t = V^{\frac{1}{2}} \sum_{k=0} (V^{\frac{1}{2}} T_o V^{\frac{1}{2}})^k V^{\frac{1}{2}}$$

which will converge if and only if

$$-1 < V^{\frac{1}{2}} T_o V^{\frac{1}{2}} < 1 \tag{3.6}$$

or simply

$$V^{-1} > -T_o \quad . \tag{3.7}$$

Using the truncation Eq. (1.30) as applied to T_o, it follows:

$$-T_o < -T_o(p) \quad . \tag{3.8}$$

Hence it is sufficient to impose

$$V^{-1} > -T_o(p) \tag{3.9}$$

to assure Eq. (3.7). Therefore a sufficient condition for the convergence of the Brillouin-Wigner series is that

$$1 > -V^{\frac{1}{2}} T_o(p) V^{\frac{1}{2}} \tag{3.10}$$

which, for $p = 0$, $To(p) = \frac{P}{\mathcal{E} - E_1^o}$, simplifies to:

$$V^{\frac{1}{2}} P V^{\frac{1}{2}} = V - V^{\frac{1}{2}} O V^{\frac{1}{2}} < E_1^o - \mathcal{E} \tag{3.11}$$

which is certainly satisfied if

$$V < E_1^o - \mathcal{E} \quad . \tag{3.12}$$

The preceding analysis is very rough; we may have some additional insight if we consider the following theorem.

Theorem 3.1.

For our operator B, a necessary and sufficient condition for $\lim_{n\to\infty} B^n = 0$ is that there exist a positive definite Hermitian operator A, for which $A - BAB^+$ is positive definite[51].

The well-known result is that $\lim_{n\to\infty} B^n = 0$ if and only if, the eigenvalues of B are all of modulus less than unity. We present here the proof of the sufficiency in theorem 3.1, as it is the result we are going to use.

Let A be any positive definite, Hermitian matrix for which

$$A - BAB^+ > 0 \quad . \tag{3.13}$$

Since $A > 0$, A can be written: $A = DD^+$ and be replaced in Eq. (3.13):

$$DD^+ - BDD^+B^+ > 0 \quad .$$

By theorem 1.3, setting $\Omega = (D^+)^{-1}$.

$$1 - KK^+ > 0 \tag{3.14}$$

where 1 is the identity operator and $K = D^{-1}BD$; this implies that the modulus of every eigenvalue of K is smaller than unity. But K is a similarity transformation of B. Hence all the eigenvalues of B are, in modulus, smaller than unity, thus $B^n \to 0$ when $n \to \infty$.

Consider now the series:

$$(A-B)^{-1} = A^{-1}\sum_{n=0}^{\infty}(BA^{-1})^n; \quad A^+ = A > 0; \quad B^+ = B < 0. \tag{3.15}$$

The power series converges iff $\lim_{n\to\infty} BA^{-1} = 0$. According to the theorem,

the series will converge iff we can find an operator C, Hermitian and positive definite such that

$$C > BA^{-1}CA^{-1}B \quad . \tag{3.16}$$

Let's set $C = A > 0$. Then the condition for convergence of Eq. (3.15) is

$$A > BA^{-1}B \quad . \tag{3.17}$$

In fact we have C entirely at our disposal. We may make other choices, for instance $C = A^2$ which yields

$$A^2 > B^2 \tag{3.18}$$

as a sufficient condition for convergence of Eq. (3.15).

Notice that Eq. (3.18) is not a trivial consequence of Eq. (3.17). Only if A and B commute, Eq. (3.18) follows from Eq. (3.17).

The relevance of these relations in BW theory follows from identifying A with V^{-1} and B with T_o. Then sufficient conditions for convergence are:

$$V^{-1} > T_o V T_o \quad \text{or} \quad 1 > (V^{\frac{1}{2}} T_o V^{\frac{1}{2}})^2 \tag{3.19}$$

which is the same condition as Eq. (3.6).

From Eq. (3.18), we obtain:

$$V^{-2} > T_o^{\,2} \quad \text{or} \quad 1 > V T_o^{\,2} V \quad . \tag{3.20}$$

Now T_o and $T_o(p)$ commute, then from $T_o > T_o(p)$ it follows $T_o^{\,2} < T_o^{\,2}(p)$, so it is sufficient to impose

$$1 > V T_o^{\,2}(p) V \tag{3.21}$$

which for p = 0 simplifies to

$$(E_1^o - \mathcal{E})^2 > VPV \tag{3.22}$$

which should be compared with Eq. (3.11). It is a better bound, though its applicability doesn't go beyond the relation in Eq. (3.12) because the best bound for VPV is $VPV < V^2$, hence Eq. (3.22) is certainly fulfilled, if $(E_1^o - \mathcal{E})^2 > V^2$ which is obtained by squaring relation Eq. (3.12).

3.2. Upper and Lower Bounds in BW Perturbation Theory

This was discussed by Löwdin in PTX. The starting point is the symmetric expansion of t:

$$t = V + VT_o + VT_o tT_o V \tag{3.23}$$

which leads to

$$t = V \sum_{k=0}^{2n-1} (T_o V)^k + (VT_o)^n t (T_o V)^n \ . \tag{3.24}$$

If $V > 0$, $\mathcal{E} < E_1^o$, we have seen that $0 < t < V$. But this means then:

$$(VT_o)^n t (T_o V)^n < (VT_o)^n V (T_o V)^n \tag{3.25}$$

and therefore

$$V \sum_{k=0}^{2n-1} (T_o V)^k V (T_o V)^k < t < V \sum_{k=0}^{2n} (T_o V)^k V (T_o V)^k \tag{3.26}$$

which is a bracketing of the operator t. In addition, it is clear that partial sums to even order in the BW expansion yield lower bounds to

the reaction operator, and odd orders provide upper bounds. If we define the functions X_k and the matrix elements ϵ_{k+1} by:

$$X_k = (T_o V)^k \psi_o ; \quad \epsilon_{k+1} = \langle \psi_o | V | X_k \rangle \quad . \tag{3.27}$$

The series in Eq. (3.2) may be written:

$$\mathcal{E}_1 = E_o^o + \sum_{k=1}^{\infty} \epsilon_k \tag{3.28}$$

where the functions X_k are defined through inhomogeneous equations. If $E_o < \mathcal{E} < E_1^o$, Eq. (3.26) leads to:

$$\mathcal{E}_1 > E_o^o + \sum_{k=1}^{2n} \epsilon_k \quad . \tag{3.29}$$

Therefore, the partial sums to even orders are lower bounds to the ground state energy, provided that $V > 0$, and $\mathcal{E} < E_1^o$. Several authors[6] have derived variational methods to obtain upper bounds to the partial sums $\sum_{k=1}^{2n} \epsilon_k$. Unfortunately, it would be more interesting to obtain lower bounds instead, because in such a case the series would still provide a rigorous lower bound to the ground state energy. The need for variational methods comes from the fact that Eq. (3.27) cannot in most cases be solved exactly for X_k. We shall discuss in the next chapter the variational methods employed in solving equations of the type in Eq. (3.27) in RS and BW theory.

Going back to Eq. (3.24), Löwdin suggested that the remainder $(VT_o)^n t (T_o V)^n$ may be replaced by an inner projection on t, $t^1 = t^{\frac{1}{2}} O t^{\frac{1}{2}}$,

in which case:

$$V \sum_{k=0}^{2n-1} (T_o V)^k + (VT_o)^n t'(VT_o)^n < T < V \sum_{k=0}^{2n} (T_o V)^k \quad . \tag{3.30}$$

He showed that a suitable choice of the inner projection leads to an estimate of the remainder in terms of quantitites already evaluated. The following formula is obtained in PTX.

$$\mathcal{E}_1 > E_o^o + \sum_{k=1}^{2n} {}_k + \alpha^+ \Delta^{-1} \alpha \tag{3.31}$$

where $\Delta_{ke} = \epsilon_{k+e+1} - \epsilon_{k+e+2}$; $(,e=0,1,2,\ldots,m-1)$ and α is a row vector of order m: $\alpha = (\epsilon_{n+1}, \epsilon_{n+2}, \ldots, \epsilon_{n+m})$.

For a given n, m = 1,2,... gives an increasing series of lower bounds, and for n = m they involve only quantities ϵ_k up to ϵ_{2n+1}. For example, if n = m = 1

$$\mathcal{E}_1 > E_o^o + \epsilon_1 + \epsilon_2 + \frac{\epsilon_2^2}{\epsilon_1 - \epsilon_2} \quad . \tag{3.32}$$

The fact remains that the quantities ϵ_k must be evaluated. Equation (3.27) means:

$$X_k = T_o V X_{k-1}, \quad X_o = \psi_o \quad . \tag{3.33}$$

Hence, by Eq. (1.7):

$$P(\mathcal{E} - H_o)X_k = PVX_{k-1}$$

or simply

$$(\mathcal{E} - H_o)X_k = VX_{k-1} - \epsilon_k \psi_o \tag{3.34}$$

and these inhomogeneous equations cannot be solved exactly. At this stage, it may be convenient to reconsider Eq. (1.46) and introduce the resolution of T_o.

3.3. Truncations of T_o in BW Theory

In what follows, ψ_o will refer to an unperturbed eigenfunction to H_o, not necessarily the ground state. We can give bounds for T_o, as indicated by Eq. (1.30). Notice that the $\bar{O}_k$'s are identical with the O_k's just because ψ_o is a single eigenfunction to H_o. Then we have, for $\mathcal{E} < E^o_{p+1}$

$$T'_o(p) \equiv \sum_{k=0}^{p}{}' \frac{O^o_k}{\mathcal{E} - E^o_k} \geq T_o \equiv \sum_{k=0}^{p}{}' \frac{O^o_k}{\mathcal{E} - E^o_k} \geq T_o(p)$$

$$\equiv \sum_{k=0}^{p}{}' \frac{O^o_k}{\mathcal{E} - E^o_k} + \frac{1}{\mathcal{E} - E^o_{p+1}} \left(1 - \sum_{k=0}^{p} O^o_k\right) \tag{3.35}$$

where the prime in the summations indicates exclusion of the term involving $O_e = |\psi^o_e\rangle\langle\psi^o_e|$ where ψ^o_e is equal to ψ_o.

Instead of solving Eq. (3.2), we may be tempted to consider instead:

$$\mathcal{E}'_1 = E^o_o + \langle\psi_o|[V^{-1} - T'_o(p)]^{-1}|\psi_o\rangle$$

$$= E^o_o + \sum_{k=0}^{\infty} \langle\psi_o|V[T'_o(p)V]^k|\psi_o\rangle \tag{3.36}$$

$$= E^o_o + \langle\psi_o|V|\psi_o\rangle + \langle\psi_o|VT'_o(p)V|\psi_o\rangle + \ldots .$$

The individual terms are easily evaluated, i.e., for ϵ_2':

$$\langle\psi_o|VT_o'(p)V|\psi_o\rangle = \sum_{k=0}^{p}{}' \frac{V_{ok}V_{ko}}{\mathcal{E} - E_k^o} = \epsilon_2' > \epsilon_2 \quad ,$$

and similarly for the higher orders. Again, we see that we get upper bounds for the second order, when it would be desirable to have a lower bound instead. Further, we do not have bounds for the higher orders. The interest of considering Eq. (3.36) at all is that we can evaluate $\mathcal{E}_1'$ to all orders by just solving an inhomogeneous equation. Consider Eq. (3.36) written in the form:

$$\mathcal{E}_1' = E_o^o + \langle\psi_o|[V^{-1} - T_o'(p)]^{-1}|\psi_o\rangle \quad . \tag{3.37}$$

Define a function X by the inhomogeneous equation:

$$[V^{-1} - T_o'(p)]^{-1}\psi_o = X \quad , \tag{3.38}$$

which may be written:

$$\psi_o = V^{-1}X - \sum_{k=0}^{p}{}' \frac{|\psi_k^o\rangle\langle\psi_k^o|X\rangle}{\mathcal{E} - E_k^o}$$

which is equivalent to the system of equations:

$$V_{eo} = C_e - \sum_{k=0}^{p}{}' \frac{V_{ek}C_k}{\mathcal{E} - E_k^o} \tag{3.39}$$

where $V_{ek} = \langle\psi_e^o|V|\psi_k^o\rangle$, $C_k = \langle\psi_k^o|X\rangle$. We are interested in C_o which is given by

$$C_o = V_{oo} + \sum_{k=0}^{P}{}' \frac{V_{ok}C_k}{\mathcal{E} - E_k^o} \quad . \tag{3.40}$$

For a given value of $\mathcal{E}$, one solves the system of linear equations in Eq. (3.39), and replaces the values of the C_k's in Eq. (3.40), thus solving Eq. (3.37) exactly. We should realize that we are not necessarily bracketing an eigenvalue of H. In fact, as

$$t^{-1} = V^{-1} - T_o \geq V^{-1} - T_o'(p) = t^{-1}(p) \tag{3.41}$$

if $t^{-1}(p) > 0$, by theorem 1.7,

$$t'(p) > t \tag{3.42}$$

and $\mathcal{E}_1'$ is an upper bound to $\mathcal{E}_1$. Therefore if $\mathcal{E}$ is an upper bound to E_o, it does not follow that $\mathcal{E}_1'$ is a lower bound. In this connection, it is interesting to study the point $\mathcal{E}_1' = \mathcal{E} = E_o'$. In order to do so, let's rewrite Eq. (3.37) in a way that makes explicit the dependence on specific states. For the state g:

$$\mathcal{E}_1'(g) = E_g^o + \langle \psi_g^o | [V^{-1} - T_o'(p)]^{-1} | \psi_g^o \rangle \tag{3.43}$$

where

$$T_o'(p) = \frac{P}{\mathcal{E} - H_o} \quad , \quad P = 1 - |\psi_g^o\rangle\langle\psi_g^o| \quad .$$

Then, we may rewrite Eq. (3.39):

$$V_{eg} = C_{eg} - \sum_{k \neq g}^{P} \frac{V_{ek}C_{kg}}{\mathcal{E} - E_k^o} \tag{3.44}$$

where $C_{eg} = \langle \psi_e^o | X_g \rangle$; $\mathcal{E}_1'(g) = E_g^o + C_{gg}$. If we impose the condition $\mathcal{E} = \mathcal{E}_1'(g)$ we obtain finally:

$$0 = C_{eg} - \sum_{k=0}^{p} \frac{V_{ek} C_{kg}}{\mathcal{E}_1'(g) - E_k^o} = - \sum_{k=0}^{p} \left\{ \frac{V_{ek}}{\mathcal{E}_1'(g) - E_k^o} - \delta_{ek} \right\} C_{kg} \,. \tag{3.45}$$

The system of equations in Eq. (3.45) has a solution if:

$$|A| = \mathrm{Det}\left[\frac{V_{ek}}{\mathcal{E}_1'(g) - E_k^o} - \delta_{ek} \right] = 0. \tag{3.46}$$

By multiplying the k^{th} column of A by $\mathcal{E}_1'(g) - E_k^o$ we obtain:

$$\prod_{k=0}^{p} (\mathcal{E}_1'(g) - E_k^o)^{-1} \, \mathrm{Det}[V_{ek} - (\mathcal{E}_1'(g) - E_k^o)\delta_{ek}] = 0.$$

But $\langle \psi_e^o | H | \psi_k^o \rangle = E_k^o \delta_{ek} + V_{ek}$, hence Eq. (3.46) is equivalent to:

$$\mathrm{Det}[H_{ek} - \mathcal{E}_1'(g)] = 0 \tag{3.47}$$

which means that the points $\mathcal{E} = \mathcal{E}_1'(g)$ are nothing but the roots of the secular equation constructed with the basis $\psi_o^o, \psi_1^o, \ldots, \psi_p^o$, and by the variational theorem they are upper bounds to the eigenvalues E_k. This shows that the truncation on the left hand side of Eq. (3.35) does not lead to very useful results for lower bounds, but it provides the explicit solution, in terms of partitioning of the secular equation in a basis of eigenfunctions to H_o.

This should not be at all surprising, because Eq. (3.47) is the secular equation arising from consideration of the truncated Hamiltonian $H'(p) = H_o'(p) + V$, where $H_o'(p) = \sum_{k=0}^{p} E_k^o O_k^o > H_o$. As $H'(p) > H$, the result

is k=0 compatible with the ordering theorem. The truncation $T_o'(p)$ or $H_o'(p)$, restricting the operators to one subspace, has as a consequence the loss of bracketing of the exact eigenvalues, unless we feed in a $\mathcal{E}$ which is a lower bound itself, but this is not a useful approach. On the other hand, the study of Eq. (3.44) provides an interesting test case for the partitioning method as applied to the solution of a secular equation. This was done by Meath, Sando, Goscinski and Hirschfelder;[52] and the preceding discussion places their work in the general framework of truncations of T_o. In the notation used in this paper, what they have done is to consider Eq. (3.44), and solve it by an iterative procedure:

$$C_{gg} = V_{gg} + \sum_{k\neq g}^{p} \frac{V_{gk}C_{kg}}{E_g^o + C_{gg} - E_k^o} . \tag{3.48}$$

By choosing a starting value for C_{gg}, the system of Eq. (3.45) can be solved for C_{kg}, which when replaced in the r.h.s. of Eq. (3.48) yields a new value for C_{gg} and the procedure is repeated till convergence. In Appendix I we present some numerical results which illustrate the convergence in terms of the derivative of an appropriate bracketing function.

A final comment should be made, and it is in regard to Eq. (3.42). We stated that if $t^{-1}(p) > 0$, Eq. (3.42) followed. The way to insure that $t^{-1}(p) > 0$, was to require $V > 0$ and $T_o'(p) < 0$, hence we should impose the condition $\mathcal{E} < E_1^o$, yet by virtue of the connection with the variational principle, we are able to arrive at the conclusion $\mathcal{E}_1'(g) \geq E_g$, in order. This points to the fact that the condition

$t^{-1}(p) > 0$ is too strong, and we were able to bypass it by solving the equations and relating them to a variational solution. We will return to this point in Chapter V, where we discuss the more interesting truncation $T_o \geq T_o(p)$

3.4. Feenberg Perturbation Theory

As we have seen in section 3.2, the convergence properties of Brillouin-Wigner perturbation theory need to be studied in considerable more detail. Morse and Feshbach[53] carry out a thorough analysis. For the present purposes we would like to point out that the convergence peculiarities derive from the power series expansion. A simple way to look at this problem is to consider Eq. (3.37). It's solution is given by Eq. (3.39) and Eq. (3.40). We may try instead a BW type expansion for Eq. (3.37). We obtain the infinite series Eq. (3.36). If we consider now the individual orders, we have for second order.

$$\mathcal{E}_2' = \langle \psi_o^o | VT_o'(p) V | \psi_o^o \rangle = \sum_{k=1}^{p} \frac{V_{ok} V_{ko}}{\mathcal{E} - E_k^o} \tag{3.49}$$

which blows up for $\mathcal{E} = E_k^o$, $k = 1,2,\ldots,p$. On the other hand, the exact solution of Eq. (3.39) is well behaved at these points, as it can be seen by rearranging it in the following way:

$$V_{eo}(\mathcal{E} - E_m^o)(\mathcal{E} - E_m^o)\ C_e - \sum_{\substack{k\neq 0 \\ k\neq m}}^{p} \frac{V_{ok} C_k}{(\mathcal{E} - E_k^o)} - V_{om} C_m .$$

Let $\mathcal{E} = E_m^o$; then $V_{om} C_m = 0$, and if $V_{om} \neq 0$, $C_m = 0$ excluding the

pathological term in Eq. (3.39). This shows that the analytical behavior of $\mathcal{E}_1'(p)$ is not reproduced accurately by the different terms of the power series expansion, and this curtails the convergence properties of the expansion. These remarks apply just as well to the BW series with T_o instead of T_o'. Let's see what happens with more detail. The third order energy in the BW series is, for the state g:

$$\epsilon_3(g) = \langle \psi_g^o | V T_o V T_o | \psi_g^o \rangle \tag{3.50}$$

and in terms of the spectral resolution:

$$\epsilon_3(g) = \sum_{\substack{k \neq g \\ e \neq g}} \frac{V_{gk} V_{ke} V_{eg}}{(\mathcal{E} - E_k^o)(\mathcal{E} - E_e^o)} \tag{3.51}$$

where there is no restriction $k \neq e$. But this means that the terms $V_{gk} V_{kg} V_{kk} / (\mathcal{E} - E_k^o)^2$ are allowed. And this type of term is unwanted. If we consider the characteristic equation of H in a basis of eigenfunctions to H_o, for a finite or an infinite basis, there should not appear any coefficient which involves products of matrix elements of the same row or column of the secular determinant:

$$\begin{vmatrix} E_o^o + V_{00} - \mathcal{E} & V_{01} & V_{02} & \cdots \\ V_{10} & E_1^o + V_{11} - \mathcal{E} & V_{12} & \cdots \\ V_{20} & V_{21} & E_2^o + V_{22} - \mathcal{E} & \cdots \end{vmatrix} = 0. \tag{3.52}$$

In Eq. (3.52), a term involving $V_{01} V_{10} V_{11}$ can not appear. Yet, as Eq. (3.51) indicates, this term will appear in the solution of $\mathcal{E}_1(g) = E_g^o + V_{gg} + \mathcal{E}_2(g) + \mathcal{E}_3(g)$.

As Feenberg[54] pointed out, these unwanted terms may be removed by what he called the rearrangement formalism. A typical term may be indicated by a diagram - see figure 4.

The diagram represents the product

$$V_{lr} V_{rt} V_{ts} V_{s2} V_{22} V_{21}$$

and the "intermediate states" 2 and s occur twice. Feenberg showed that it is possible to eliminate the repeated terms if one modifies the denominators in the BW series. There are several ways to go about this. Feenberg's rearrangement formalism[54], Bisshopp's[55] asymptotic approximation to a Fredholm type solution and Morse and Feshbach's treatment, based on the expansion of the characteristic equation. Kumar[19] introduces a rearrangement operator and a "Feenberg potential" in order to derive the equations which seems a bit too dangerous, considering that the equations are nothing but a rearrangement. In fact, we intend to show that they can be derived by the successive partitioning technique discussed by Nordling[56]. The significance of this is important. The partitioning technique, PT, pursues the solution of the secular equation via a successive partitioning technique, SPT. A complete solution of the system of equations is not performed, only a first triangularization of the solution being needed. We shall show this in the next section where we will prove that SPT applied to Eq. (3.44) yields the p^{th} approximant to Feenberg's perturbation scheme, to which it is entirely equivalent.

We shall review several derivation of Feenberg's formalism and then present the successive partitioning derivation which illuminates

some properties of the method, in particular the connection with the continued fraction representation of the solutions.

Kumar[19] defines P_F, the Feenberg operator, to be such, that in the expansion of $\langle \psi_g^o | P_F t_F | \psi_g^o \rangle$, the state ψ_g^o is not equal to any intermediate state, and where t_F is a modified reaction operator, involving the Feenberg potential, which he defines as $V_F = \sum_k \langle t_F \rangle_{kk} O_k^o$. So, the operator being considered is, by making the formal translation into the language employed in this dissertation

$$t_F = V + V \frac{P_F}{\mathcal{E} - H_o - V_F} t_F \quad . \tag{3.53}$$

This definition, which should be compared with Eq. (1.44a) implies the following expansion:

$$t_F = V + V \frac{P_F}{\mathcal{E} - H_o - V_F} V + V \frac{P_F}{\mathcal{E} - H_o - V_F} V \frac{P_F}{\mathcal{E} - H_o - V_F} V + \ldots \; .$$

If we use the spectral resolution of the operator $\frac{P_F}{\mathcal{E} - H_o - V_F}$

and noticing that the definition of V_F entails that

$$H_o + V_F = \sum_k [E_k^o + \langle t \rangle_{kk}] O_k^o,$$

we obtain

$$t_F = V + \sum_{k \neq o} \frac{V O_k^o V}{\mathcal{E} - E_k^o - \langle t_F \rangle_{kk}} + \sum_{\substack{k \neq o \\ \ell \neq o, \ell \neq k}} \frac{V O_k^o V O_\ell^o V}{(\mathcal{E} - E_k^o - \langle t_F \rangle_{kk})(\mathcal{E} - E_\ell^o - \langle t_F \rangle_{\ell\ell})} \tag{3.54}$$

$$+ \sum_{\substack{k \neq o \\ \ell \neq o, k \\ \ell m \neq o, k,}} \frac{V O_k^o V O_\ell^o V O_m^o V}{(\mathcal{E} - E_k^o - \langle t_F \rangle_{kk})(\mathcal{E} - E_\ell^o - \langle t_F \rangle_{\ell\ell})(\mathcal{E} - E_m^o - \langle t_F \rangle_{mm})} + \ldots \; .$$

The effect of P_F is to impose the injunctions on the indices of summation. If we use the following notations:

$$(\lambda^2)_{pqr\ldots,n} = E_n^o + \langle t_F \rangle_{nn}, \quad \begin{matrix} n \neq p,q,r,s\ldots \\ p \neq q,r,\ldots \\ q \neq r,s\ldots \end{matrix} \qquad (3.55)$$

Eq. (354) may be rewritten:

$$t_F = V + \sum_{k\neq o} \frac{Vo_k^o V}{\mathcal{E} - (\lambda^2)_{o,k}} + \sum_{\substack{k\neq o \\ \ell\neq o,k}} \frac{Vo_k^o Vo^o V}{[\mathcal{E} - (\lambda^2)_{o,k}][\mathcal{E} - (\lambda^2)_{ok,\ell}]}$$

$$+ \sum_{\substack{k\neq o \\ \ell\neq o,k \\ m\neq o,k,\ell}} \frac{Vo_k^o Vo_\ell^o Vo_m^o V}{[\mathcal{E} - (\lambda^2)_{o,k}][\mathcal{E} - (\lambda^2)_{ok,\ell}][\mathcal{E} - (\lambda^2)_{ok\ell,m}]} + \ldots \quad . \qquad (3.56)$$

Feenberg's perturbation series follows from Eq. (3.56) by setting $\mathcal{E}_1 = \mathcal{E} = E$ in:

$$\mathcal{E}_1 = E_o^o + \langle t_F \rangle_{oo} = E_o^o + \langle \psi_o^o | t_F | \psi_o^o \rangle \quad . \qquad (3.57)$$

The burden of the proof now is to establish that $\langle t_F \rangle_{oo} = \langle t \rangle_{oo}$. One should realise that this is very formal, and the Feenberg operator may not be definable for all states appearing in the expansion Eq. (3.57). So instead of reproducing Kumar's proof, which is subject to criticism, we shall point out that Eq. (3.57) may be rewritten in the form:

$$\mathcal{E}_1 = E_o^o + V_{oo} + \sum_{k\neq o} \frac{V_{ok} V_{ko}}{\mathcal{E} - (\lambda^2)_{o,k}} + \sum_{\substack{k\neq o \\ \ell\neq o,k}} \frac{V_{ok} V_{k\ell} V_{\ell o}}{[\mathcal{E} - (\lambda^2)_{o,k}][\mathcal{E} - (\lambda^2)_{ok,\ell}]}$$

$$+ \ldots\ldots \qquad (3.58)$$

where

$$(\lambda^2)_{o,k} = E_k^o + V_{kk} + \sum_{\ell \neq o,k} \frac{V_{k\ell} V_{\ell k}}{\mathcal{E} - (\lambda^2)_{ok,\ell}} + \sum_{\substack{\ell \neq o,k \\ m \neq o,k,\ell}} \frac{V_{k\ell} V_{\ell m} V_{mk}}{[\mathcal{E} - (\lambda^2)_{ok,\ell}][\mathcal{E} - (\lambda^2)_{ok\ell,m}]} + \ldots \tag{3.59a}$$

and similarly:

$$(\lambda^2)_{ok,\ell} = E_\ell^o + V_{\ell\ell} + \sum_{m \neq o,k,\ell} \frac{V_{\ell m} V_{m\ell}}{\mathcal{E} - (\lambda^2)_{ok\ell,m}} + \sum_{\substack{m \neq o,k,\ell \\ n \neq o,k,\ell,m}} \frac{V_{\ell m} V_{mn} V_{n\ell}}{[\mathcal{E} - (\lambda^2)_{ok\ell,m}][\mathcal{E} - (\lambda^2)_{ok\ell m,n}]} \tag{3.59b}$$

and so on.

It is quite clear that the expansion in Eq. (3.58) with the denominators in Eqs. (3.59a) and (3.59b) seems to fulfill the requirement that no coefficient has products of terms V_{ij} with repeated indices, i.e., terms that are forbidden in the expansion of a secular equation. In fact, as Feshbach[57] has shown, the Eqs. (3.58) and (3.59) represent the exact solution, by elimination, of the system of linear equations whose solution is determined by the secular Eq. (3.52). In other words, given an infinite secular equation, or a finite one, the eigenvalues are given by Eqs. (3.58) and (3.59). If the basis is finite the injunctions on the indices in Eq. (3.54) imply that there will be a finite number of terms in such an expansion, in fact it is easy to

see that for an N dimensional basis, the zth order in the expansion of Eq. (3.54) has $\beta(N,z) = (N-1)(N-2)\ldots(N-z+1)$ terms in the sum, hence in the expansion Eq. (3.54), the orders N+1 and higher are vanishing. The fact that Eq. (3.58) can be obtained from the characteristic equation constitutes a proof of Feenberg's expansion and of the formal validity of the expansion obtained by Kumar. If we apply this elimination to Eq. (3.37), we will obtain a Feenberg type series with contributions through p^{th} order. That elimination can be carried out explicitly and yields an expression not too wieldy for computational purposes, and Eq. (3.37) seems preferable. The advantages of Feenberg's scheme are apparent for certain cases that we will discuss in the next section. The point is that any finite approximant M_p to the Feenberg series in Eq. (3.54), which consists of summations over k,ℓ,m, etc., with $0 < k \leq p$, and injunctions on the indices, has N orders, each of which consists of a finite sum of terms, and it rigorously yields a solution to a variational secular equation, thus, it gives an upper bound. So far the index "o" has not been specified and this means that we can obtain any of the first p+1 states by setting "o" equal to the ground state, first excited state, etc. The approximants M_p were obtained by Bisshopp[55] in a different way, but we want to emphasize their variational connotations, and absence of convergence problems in this case.

There is an entirely different derivation, given by Feenberg[54] based on transformations of the BW series which amounts to a rearrangement of the series. He employed a set of algebraic identities, originally due to Richards[58] and by very interesting manipulations, the series in Eq. (3.54) is obtained.

The wave function itself is obtained too, with expansions for the coefficients, as given by Morse and Feshbach. We shall omit a discussion of the convergence properties of the series, to concentrate on the features of the elimination approach that led to Eq. (3.58). A secular equation, finite or infinite, is a condition for the existence of solutions of a system of homogeneous equations. The elimination procedure can be related to partitioning, and that is what we discuss in the next section.

3.5. Successive Partitioning Technique and Perturbation Schemes

For simplicity we shall consider first the Schrödinger equation

$$\mathbb{H}\,\mathbb{C} = E\,\mathbb{C} \tag{3.60}$$

which can be written

$$\mathbb{M}\mathbb{C} = 0, \quad \mathbb{M} = \mathbb{H} - E\mathbb{I} \quad . \tag{3.61}$$

Conventional partitioning technique, as discussed in the PT series implies that we can partition Eq. (3.61) into four blocks, corresponding to two subspaces, "a" and "b", thus obtaining the equations:

$$[M_{aa} - M_{ab} M_{bb}^{-1} M_{ba}]\mathbb{C}_a = 0 \tag{3.62}$$

$$\mathbb{C}_b = - M_{bb}^{-1} M_{aa} \cdot \mathbb{C}_a \quad . \tag{3.63}$$

Conventional partitioning technique corresponds to choosing subspace "a" as one dimensional, in which case we obtain:

$$[M_{11} - M_{1b} M_{bb}^{-1} M_{b1}]C_1 = 0$$

which for $C_1 \neq 0$ implies:

$$\mathcal{E}_1 = H_{11} + H_{1b}(\mathcal{E}\mathbb{1}_{bb} - H_{bb})^{-1}H_{b1} \quad . \tag{3.64}$$

This equation should be compared with Eq. (1.12). In fact, Eq. (1.12) is nothing but the same equation in operator form when the subspace "b" is the orthogonal complement of "a". That is, when we deal, in principle, with an infinite-dimension secular equation. But going back to Eq. (3.64), we can establish the bracketing theorem for $\mathcal{E}_1 = f(\mathcal{E})$. See PTI and PTII. This has been thoroughly discussed in Chapter I. A very interesting alternative is given by choosing subspace "b" as being one-dimensional. In such a case, $M_{bb} = M_{NN}$, and $\mathbb{C}_b = C_N$. Equation (3.62) is now:

$$\left(M_{aa} - \frac{M_{aN}M_{Na}}{M_{NN}^{-1}} \right) \mathbb{C}_a = 0 \quad . \tag{3.65}$$

We have reduced the order of Eq. (3.61) by one, and this may be done again. In fact, we may define a series of reductions, by successive partitioning, until we obtain a one-dimensional problem. We will use the notation introduced by Nordling[56] and define the following:

$$\begin{aligned} \mathbb{M}^{(N)} &= \mathbb{M} \\ \mathbb{M}^{(i-1)} &= \mathbb{M}_{aa}^{(i)} - \frac{\mathbb{M}_{ai}^{(i)}\mathbb{M}_{ia}^{(i)}}{M_{ii}^{(i)}} \quad , \quad i = N, N-1, \ldots, \beta. \end{aligned} \tag{3.66}$$

where

$$\mathbb{M}^{(i)} = \begin{bmatrix} \mathbb{M}_{aa}^{(i)} & \mathbb{M}_{ai}^{(i)} \\ \mathbb{M}_{ia}^{(i)} & M_{ii}^{(i)} \end{bmatrix} \quad . \tag{3.67}$$

That is, $M^{(i)}$ is a square matrix of order i, $M_a^{(i)}$ is its upper left square part, of order i-1, etc. The vectors $C^{(i)}$ are defined as follows:

$$C^{(N)} = C$$

$$C^{(i-1)} = C_a^{(i)} \qquad i = N,N-1,\ldots,2 \qquad (3.68)$$

$$C^{(i)} = \begin{vmatrix} C_a^{(i)} \\ c_i^{(i)} \end{vmatrix}$$

where $C_a^{(i)}$ is the column vector formed by the first i-1 components of the column vector $C^{(i)}$.

The successive partitioning amounts to replace Eq. (3.61) by the sequence of eigenvalue problems:

$$M^{(i)}C^{(i)} = 0 \qquad i = N,N-1,\ldots,1 \ . \qquad (3.69)$$

We are interested in the last equation of the sequence:

$$M^{(1)}C^{(1)} = 0 \qquad (3.70)$$

$$[E - H^{(1)}]C^{(1)} = 0 \qquad (3.71)$$

which, for $C^{(1)} \neq 0$ is equivalent to:

$$E = H^{(1)} = h(E) \qquad (3.72)$$

where E is an eigenvalue of Eq. (3.60). Actually, we should consider the equation

$$\mathcal{E}_1 = h(\mathcal{E}) \qquad (3.73)$$

and compare it with $\mathcal{E}_1 = f(\mathcal{E})$ given by Eq. (3.64).

We want to prove that $h(\mathcal{E})$ and $f(\mathcal{E})$ are one and the same function, and that the only difference between Eqs. (3.73) and (3.64) is that the former corresponds to a triangularization of the system of equations (3.63) with $C_a = C_1$, necessary to compute Eq. (3.64). We have met an example of a system of linear equations of this type before, namely, Eq. (3.44).

Before proving $\mathcal{E}_1 = f(\mathcal{E}) = h(\mathcal{E})$ we should remark that once the eigenvalue E has been found, the eigenvector can be obtained by setting $C_1 = 1$, or any other constant, and performing the sequence of operations:

$$\begin{aligned} \mathbb{C}_a^{(i)} &= \mathbb{C}^{(i-1)} \\ C_i^{(i)} &= \frac{M_{ia}^{(i)} \mathbb{C}_a^{(i)}}{M_{ii}^{(i)}} \\ \mathbb{C}_i &= \begin{bmatrix} \mathbb{C}_a^{(i)} \\ C_i^{(i)} \end{bmatrix} \end{aligned} \qquad (3.74)$$

The proof follows from the fact that the successive partitioning scheme, as defined by Eq. (3.68) corresponds to a triangularization of a system of equations. Consider, for instance, the system of equations

$$\mathbb{M}\mathbb{C} = \mathbb{D} \qquad (3.75)$$

A lower triangularization of this system amounts to transform it into:

$$\mathbb{M}'\mathbb{C} = \mathbb{D}' \qquad (3.76)$$

where M' is a lower triangular matrix, i.e., all its elements above

the diagonal are zero. The connection of Eq. (3.76) with Eq. (3.69) follows from the fact that the i^{th} row of $\mathbb{M}'$ is defined by the last row of $\mathbb{M}^{(i)}$, and d'_i, the i^{th} element of the column vector $\mathbb{d}'$ is given by the last element of the vector $\mathbb{d}^{(i)}$, defined as follows:

$$\begin{aligned} \mathbb{d}^{(N)} &= \mathbb{d} \\ \mathbb{d}^{(i)} &= \begin{bmatrix} \mathbb{d}_a^{(i)} \\ d_i^{(i)} \end{bmatrix} \qquad i = N, N-1, \ldots, 2 . \\ \mathbb{d}^{(i-1)} &= \mathbb{d}_a^{(i)} - \frac{\mathbb{M}_{ai}^{(i)} d_i}{M_{ii}^{(i)}} \end{aligned} \tag{3.77}$$

Once Eq. (3.70) is obtained, the solution of Eq. (3.74) follows from:

$$\begin{aligned} C_1 &= \frac{d_1^{(1)}}{M_{11}^{(1)}} \\ C_i &= d_i^{(i)} - \frac{M_{ia} \mathbb{C}^{(i-1)}}{M_{ii}^{(i)}} \\ \mathbb{C}^{(i)} &= \begin{bmatrix} \mathbb{C}^{(i-1)} \\ C_i \end{bmatrix} \end{aligned} \qquad . \tag{3.78}$$

Consider now the problem $\mathbb{M}\mathbb{C} = 0$. It is of the type in Eq. (3.75), with $\mathbb{d} = 0$. If we carry the first N-2 of the N-1 steps indicated by Eq. (3.71), we obtain:

$$\mathbb{M}'\mathbb{C} = 0 \tag{3.79}$$

where the last N-1 rows and last N-1 columns of $\mathbb{M}'$ are in lower triangular form. In fact, we can write the last N-1 rows of Eq. (3.79) as

$$M'_{bb}C_b = - M'_{b1}C_1 \tag{3.80}$$

where M'_{bb} is lower triangular.

The first row of Eq. (3.61) can be written:

$$M_{11}C_1 + M_{1b}C_b = 0 \quad . \tag{3.81}$$

Under the transformations that lead to Eq. (3.79) it becomes:

$$M^{(2)}_{11}C_1 + M^{(2)}_{12}C_2 = 0 \quad .$$

For $C_1 = 1$, it is simply:

$$E = H^{(2)}_{11} + M^{(2)}_{12}C_2 \quad . \tag{3.82}$$

From Eq. (3.78)

$$C_2 = - \frac{M^{(2)}_{21}}{M^{(2)}_{22}}$$

and then

$$E = H^{(2)}_{11} - \frac{M^{(2)}_{12}M^{(2)}_{21}}{M^{(2)}_{22}} = h(E) \quad . \tag{3.83}$$

This is clearly the result from successive partitioning technique, as determined by Eq. (3.72). Thus, the elimination technique leading to a triangularization of Eq. (3.61) is identical to the successive partitioning scheme. Furthermore, we may consider the partitioning equation (3.64) written in the following way:

$$E = H_{11} + M_{1b}C_b = f(E) \tag{3.84}$$

with C_b given by the system of N-1 linear equations:

$$M_{bb}C_b = - M_{b1} \quad . \tag{3.85}$$

The N-1 transformations leading to Eq. (3.79), and hence to Eq. (3.83), do nothing but carry out a triangularization of Eq. (3.85); no change in the nature of the solution, but a somehow simplified form of the equations is obtained, which when solved and substituted in Eq. (3.84) yields the partitioning solution f(E). Now, not only f(E) = h(E), but in general, $f(\mathcal{E}) = h(\mathcal{E})$ holds. One way of seeing this is to expand the denominators in Eq. (3.58), obtaining the Brillouin series, which may be summed up again to yield the conventional partitioning expression. Of course, for finite N the expansion of $h(\mathcal{E})$ given by Eq. (3.58) can be transformed back into a system of linear equations of the type in Eq. (3.44). In the case of an infinite basis, the elimination procedure can be considered as being possible in a formal sense. The equations are derived by mathematical induction, as shown by Morse and Feshbach and the same considerations apply to the successive partitioning approach. This last approach, as well as the observation that no term involving V_{ss} appears in the sums in Eq. (3.58) implies that the matrix elements of V may be replaced by matrix elements of H.

We went into the successive partitioning scheme with considerable detail because it illuminates some aspects of the Feenberg approach. From

$$f(\mathcal{E}) = h(\mathcal{E}) \quad , \tag{3.86}$$

it follows

$$0 \geq f'(\mathcal{E}) = h'(\mathcal{E}) \quad . \tag{3.87}$$

The importance of this result is quite apparent. The Feenberg perturbation expansion, given by Eqs. (3.58) and (3.59) is a bracketing function, namely that $\mathcal{E}_1$ and $\mathcal{E}$ bracket one eigenvalue

of H. If one has a finite approximant, i.e., with a finite number of orders included, the solution to $E = f(E)$ is bracketed, but this is not the exact eigenvalue, but an upper bound to it. Actually one is not interested in finite approximants to the Feenberg series, but in the infinite expansions. The reason for it is that they assume particularly useful forms under special circumstances, and these can be discussed in terms of the properties of successive partitioning. As pointed out by Nordling[56], successive partitioning of a triple diagonal matrix has a very simple form. By triple diagonal matrix, we mean a matrix

$$T = \begin{vmatrix} \alpha_1 & \beta_2 & 0 & . & . & . & . \\ \beta_2 & \alpha_2 & \beta_3 & 0 & . & . & . \\ 0 & \beta_3 & \alpha_3 & \beta_4 & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & 0 & \beta_N & \alpha_N \end{vmatrix} . \qquad (3.88)$$

For any symmetric real matrix it is possible to define a unitary transformation which brings it into triple diagonal form. Many matrices corresponding to physical problems are already in this form: systems with nearest neighbour interaction. There are equations where the nature of the perturbation is such that it has a triple diagonal form automatically, i.e., the Mathieu prblem, the anharmonic oscillator with $V = \lambda X$. Actually the matrix corresponding to the Mathieu problem is "triple diagonal" but with a string of zeroes between the main diagonal and the two parallel strings of non-vanishing elements; this is due to the fact that $V_{nm=o}$ unless $m = n \pm 2$ or $m = n$. Consider then, in general, a triple diagonal matrix with k strings of zeroes separating

the strings of non-zero components. We can generalize the scheme defined by Eq. (3.66) and obtain an explicit solution via successive partitioning, in terms of a continued fraction for an infinite matrix, or in terms of a truncated continued fraction for any finite problem. This corresponds to an extension of Nordling's scheme. The observation of the continued fraction representation leads to compact derivation of several properties of this type of solution.

In terms of Eq. (3.66) define:

$$\mathbb{D}^{(i)} = \frac{M_{a,i+1}^{(i+1)} M_{i+1,a}}{M_{i+1,i+1}^{(i+1)}} \quad . \tag{3.89}$$

For any triple diagonal matrix of the types discussed above, the matrix $\mathbb{D}^{(i)}$ has only one non-vanishing element. If there are k strings of zeroes between the diagonal and the two parallels of non-zero matrix elements, the non-vanishing components of $\mathbb{D}^{(i)}$ will be:

$$D_{i-k,i-k}^{(i)} = \frac{M_{i-k,i+1}^{(i+1)} M_{i-k,i+1}^{(i+1)}}{M_{i+1,i+1}^{(i+1)}} \quad , \quad i = N-1, N-2, \ldots, k+1. \tag{3.90}$$

To make this clear, we shall use the following notation

$$\mathbb{T} = \begin{vmatrix} \alpha_1 & 0 & 0 & \beta_4 & 0 & 0 & \cdots \\ 0 & \alpha_2 & 0 & 0 & \beta_5 & 0 & \cdots \\ 0 & 0 & \alpha_3 & 0 & 0 & \beta_6 & \cdots \\ \beta_4 & 0 & 0 & \alpha_4 & 0 & 0 & \cdots \end{vmatrix} \tag{3.91}$$

where we have depicted the case k = 2.

Then Eq. (3.90) can be written:

$$D^{(i)}_{i-k,i-k} = \frac{\beta^2_{i+1}}{\alpha^{(i+1)}_{i+1} - E} \quad , \quad i = N-1, N-2, \ldots, k+1 \tag{3.92}$$

where $\alpha^{(i)}_i$ is given by:

$$\alpha^{(i-k)}_{i-k} = \alpha^{(i)}_{i-k} = \alpha_{i-k} - D^{(i)}_{i-k,i-k'} \quad i = N-1, N-2, \ldots, k+1. \tag{3.93}$$

Equation (3.93) states simply that when we carry the successive partitioning corresponding to Eq. (3.66), if the matrix is triple diagonal, only one diagonal element in the subspace $\underline{a}$ is going to be changed. The process indicated by Eq. (3.93) is carried until we obtain

$$E = h(E) = \alpha^{(k+1)}_1 \quad . \tag{3.94}$$

What we want to stress is that Eq. (3.94) can be used, in conjunction with Eqs. (3.93) and (3.92) to construct an explicit solution by "back" iteration:

From Eqs. (3.94) and (3.93):

$$E = h(E) = \alpha^{(k+1)}_1 = \alpha_1 - D^{(k+1)}_1$$

and using Eq. (3.92):

$$E = \alpha_1 - \frac{\beta^2_{k+2}}{\alpha^{(k+2)}_{k+2} - E} = \alpha_1 + \frac{\beta^2_{k+2}}{E - \alpha_{k+2}} = \alpha_1 + \frac{\beta^2_{k+2}}{E - \alpha^{(2k+2)}_{k+2}} \tag{3.95}$$

$$= \alpha_1 + \frac{\beta^2_{k+2}}{E - \alpha_{k+2} + D^{(2k+2)}_{k+2,k+2}} = \alpha_1 + \frac{\beta^2_{k+2}}{E - \alpha_{k+2} + \dfrac{\beta^2_{2k+3}}{\alpha^{(2k+3)}_{2k+3} - E}} \quad .$$

Let's consider, for example, the case k = 0. This is the conventional triple diagonal matrix case:

$$T = \begin{vmatrix} \alpha_1 & \beta_2 & 0 \cdots \\ \beta_2 & \alpha_2 & \beta_3 \cdots \\ 0 & \beta_3 & \alpha_3 \ \beta_4 \cdots \\ \cdots\cdots\cdots\cdots\cdots \end{vmatrix} \tag{3.96}$$

The first eigenvalue is given by:

$$E = \alpha_1 + \cfrac{\beta_2^2}{E-\alpha_2 - \cfrac{\beta_3^2}{E-\alpha_3 - \cfrac{\beta_4^2}{E - \alpha_4 - \cdots\cdots}}} \tag{3.97}$$

As pointed out by Nordling[56], any NxN symmetric real matrix H can be transformed into the form of Eq. (3.96) by a unitary transformation. Hence Eq. (3.97) is the explicit representation of the first eigenvalue. Of course, suitable modifications of Eq. (3.97) hold for other eigenvalues. Equation (3.97) is valid for an infinite matrix of the form in Eq. (3.96) in which case it provides a continued fraction type of solution. In either case, we want to stress the importance of the continued fraction solution obtained by the "back" iteration in Eq. (3.95), because it provides fast numerical convergence and because the formal properties of continued fractions, like recurrence relations, etc., give a simple explanation of the properties of triple diagonal matrices, their determinants and eigenvalues, and this is certainly an alternate path to the one discussed by Nordling.

Applications of the Feenberg scheme are interesting when the matrices are triple diagonal, but in these cases the continued fraction solutions are a natural tool, which follows from successive partitioning. When the matrices are not triple diagonal, the possibility of implementing Feenberg's scheme relies on finite approximants, which are related to the variational principle, suggesting that other schemes may be equally or more useful, in fact, the truncations of T_o discussed in Chapter V and the applications of the techniques of PTX are more interesting in terms of usefulness. On the other hand, the continued fraction solutions, for problems with nearest neighbour interactions should prove very useful.

CHAPTER IV

RECIPROCAL VARIATIONAL PROBLEMS AND PERTURBATION THEORY

The implementation of conventional perturbation theory requires the computation of the individual orders, both in BW and RS theory. Exact evaluation involves an infinite sum and an integration over the continuum when using a resolvent technique; solution of an inhomogeneous equation is the alternative, not easily attainable in most cases. Thus the need for approximate solutions, which are of variational type. These may be very successful, but we should emphasize that only through computation of upper and lower bounds to the individual orders, something may be said about the nature of the approximation.

Hylleraas[59] was the first to derive a variational expression for the second order energy in RS theory, giving an upper bound to it. In fact, as the inhomogeneous equations that characterize the different orders in RS and BW theory can be related to variational principles, it turns out that the even order energies have upper bounds given by functionals. The minimization yields an upper bound to the even order energy and a function that can be used to compute approximations to the other orders. Knight and Scherr[60] exploited this in the He series. Midtal[61] discussed the orthogonality properties that explain their success. Prager and Hirschfelder[7] obtained an expression for a lower bound to the ground state second order perturbation energy in the RS

scheme and this was generalized by Sando and Hirschfelder[62]. Meath and Hirschfelder[63] obtained variational upper bounds in the BW scheme, similar to the Hylleraas principle. Sinanoğlu[64] stated an orthogonality requirement towards the lower unperturbed eigenfunctions which allows extension of the Hylleraas principle to excited states, and this was carried out for the BW case in reference 63.

Hirschfelder and Prager derived their formula by analogy with electromagnetic theory. We shall introduce the geometric language of Synge[8], in the case of positive metric, and then show that special choices lead to the Hylleraas principle and to the Hirschfelder and Prager formula in a natural way.

4.1. Reciprocal Variational Problems

Consider a linear vector space $\mathcal{L}$, with vectors $\underline{p}$. We don't specify their nature at all; they may be functions, or sets of functions. Consider a Hermitian positive metric in the space $\mathcal{L}$, defined by

$$Q(\underline{p},\underline{p}) \geq 0 \tag{4.1}$$

where the equality sign holds if and only if $\underline{p} = 0$.

Consider two linear subspaces of $\mathcal{L}$; Σ and Ω. We will say that they are orthogonal if and only if for all $\underline{\sigma} \in \Sigma$ and all $\underline{\omega} \in \Omega$

$$Q(\underline{\sigma},\underline{\omega}) = 0 \quad . \tag{4.2}$$

If we interpret $Q(\underline{p},\underline{p})$ as the square of the norm of $\underline{p}$, a "Pythagorean theorem" is fulfilled:

$$Q(\underline{\omega}-\underline{\sigma},\underline{\omega}-\underline{\sigma}) = Q(\underline{\omega}+\underline{\sigma},\underline{\omega}+\underline{\sigma}) = Q(\underline{\omega},\underline{\omega}) + Q(\underline{\sigma},\underline{\sigma}) \quad . \tag{4.3}$$

Within this context define two variational problems:

I) Given two vectors $\underline{p}_o$ and $\underline{q}_o$, a linear subspace Ω and its orthogonal complement Σ, minimize

$$d_1(\underline{p}) = Q(\underline{p}-\underline{q}_o, \underline{p}-\underline{q}_o) \tag{4.4}$$

with the constraint that $\underline{p} - \underline{p}_o$ should belong to Ω.

II) For the same $\underline{p}_o, \underline{q}_o$, Ω and Σ as before, minimize

$$d_2(\underline{q}) = Q(\underline{q}-\underline{p}_o, \underline{q}-\underline{p}_o) \tag{4.5}$$

subject to the constraint that $\underline{q} - \underline{q}_o$ should belong to Σ.

These two variational problems have some properties of interest, easily derived. Let $\underline{u}$ be the solution of Problem I, i.e., it minimizes Eq. (4.4). Then consider a specific $\underline{p}$, of the form:

$$\underline{p}_1 = \underline{u} + \epsilon\underline{\omega} \tag{4.6}$$

for real ϵ and any $\underline{\omega} \in \Omega$. Substitute Eq. (4.6) into Eq. (4.4), and set the first variation of ϵ equal to zero.

$$d_1(\underline{p}_1) = Q(\underline{p}_1, \underline{p}_1) = Q(\underline{u}+\epsilon\underline{\omega}-\underline{q}_o, \underline{u}+\epsilon\underline{\omega}-\underline{q}_o)$$

$$\delta d_1(\underline{p}_1) = 2Q(\underline{\omega}, \underline{u}) - 2Q(\underline{\omega}, \underline{q}_o) = 0$$

which may be written

$$Q(\underline{u}, \underline{q}_o, \underline{\omega}) = 0. \tag{4.7}$$

This consists

Theorem 4.1:

The necessary condition for Problem I to have a solution is that $\underline{u} - \underline{q}_o$ should belong to Σ. Notice that this is precisely the constraint of Problem II.

Theorem 4.2:

$\underline{u}$ is unique. The proof consists in assuming two solutions $\underline{u}_1$ and $\underline{u}_2$. Then $\underline{u}_1 - \underline{q}_o \in \Sigma$, and $\underline{u}_2 - \underline{q}_o \in \Sigma$. Hence, $\underline{u}_1 - \underline{u}_2 \in \Sigma$. But the constraint of Problem I imposes $\underline{u}_1 - \underline{p}_o \in \Omega$, $\underline{u}_2 - \underline{p}_o \in \Omega$ and hence $\underline{u}_1 - \underline{u}_2 \in \Omega$. This means that $\underline{u}_1 - \underline{u}_2$ belongs to the intersection of Σ and Ω, which are orthogonal subspaces, and therefore contains only the zero vector. Therefore $\underline{u}_1 = \underline{u}_2$. Q.E.D.

The following two theorems have entirely similar proofs:

Theorem 4.3:

The necessary condition for Problem II to have a solution is that $\underline{v} - \underline{p}_o$ is in Ω, where $\underline{v}$ is the vector that minimizes Eq. (4.5). Notice that this is the constraint of Problem I.

Theorem 4.4:

$\underline{v}$ is unique.

The significant result in this context is:

Theorem 4.5:

$$\underline{u} = \underline{v} .$$

Proof:

$\underline{u} - \underline{q}_o \in \Sigma$ (Theorem 4.1).

$\underline{v} - \underline{q}_o \in \Sigma$ (Constraint of Problem II).

Hence

$$\underline{u} - \underline{v} \in \Sigma.$$

Similarly

$\underline{v} - \underline{p}_o \in \Omega$ (Theorem 4.3)

$\underline{u} - \underline{p}_o \in \Omega$ (Constraint of Problem I).

Then

$$\underline{u} - \underline{v} \in$$

and it follows that $\underline{u} - \underline{v}$ must be the zero vector. Q.E.D.

Theorem 4.6:

Let d_1, d_2 be the minima of Problems I and II, respectively. Then: $d_1 + d_2 = Q(\underline{p}_o - \underline{q}_o, \underline{p}_o - \underline{q}_o)$.

Proof:

$$d_1 + d_2 = Q(\underline{u} - \underline{q}_o, \underline{u} - \underline{q}_o) + Q(\underline{u} - \underline{p}_o, \underline{u} - \underline{p}_o) \ .$$

By the Pythagorean relation in Eq. (4.3):

$$d_1 + d_2 = Q(\underline{u} - \underline{q}_o - \underline{u} + \underline{p}_o, \underline{u} - \underline{q}_o - \underline{u} + \underline{p}_o) = Q(\underline{p}_o - \underline{q}_o, \underline{p}_o - \underline{q}_o). \quad \text{Q.E.D.}$$

The sum of the minima of the two reciprocal problems, I. and II, is then exclusively determined by $\underline{p}_o$ and $\underline{q}_o$. We say reciprocal because the constraint of one problem is the Euler condition of the other and vice versa. The following theorem also holds, and is the key to the applications:

Theorem 4.7:

The sphere of radius $\left| \frac{\underline{p} - \underline{q}}{2} \right|$ about the point $\frac{\underline{p} + \underline{q}}{2}$ is a geometrical locus of $\underline{u}$.

The proof follows from consideration of

$$\begin{aligned} 4Q\left(\underline{u} - \frac{\underline{p}+\underline{q}}{2}, \underline{u} - \frac{\underline{p}+\underline{q}}{2}\right) &= Q(\underline{u} - \underline{p} + \underline{u} - \underline{q}, \underline{u} - \underline{p} + \underline{u} - \underline{q}) = Q(\underline{u} - \underline{p}, \underline{u} - \underline{p}) \\ &+ Q(\underline{u} - \underline{q}, \underline{u} - \underline{q}) = Q(\underline{u} - \underline{q} - (\underline{u} - \underline{p}), \underline{u} - \underline{q} - (\underline{u} - \underline{p})) = Q(\underline{p} - \underline{q}, \underline{p} - \underline{q}) \ . \end{aligned} \tag{4.8}$$

The third line in Eq. (4.8) follows from the orthogonality of $\underline{u} - \underline{p}$ and $\underline{u} - \underline{q}$, and the fourth line too, bu successive application of the

"Pythagorean Theorem" in Eq. (4.3). But Eq. (4.8) is precisely theorem 4.7, as it can be seen by dividing through by four:

$$\left| u - \frac{p+q}{2} \right| = \left| \frac{p-q}{2} \right| \quad . \tag{4.9}$$

We can restate the theorem. The common solution to the reciprocal Problems I and II deviates from the arithmetic mean of two trial vectors $\underline{p}$ and $\underline{q}$, satisfying the constraints for Problems I and II, respectively, by an amount equal to half the distance between the two vectors $\underline{p}$ and $\underline{q}$. This is nothing but a version of the theorem of Thales, as it can be seen from Figure 5.

Equation (4.9) constitutes an estimate of the norm accuracy of the trial vectors, p and g; for the reciprocal Problems I and II. Theorem 4.6, has the important consequence that an upper bound for one problem constitutes a lower bound to it's reciprocal, since the sum of the two minima, $d_1 + d_2$, is given in the specification of the problems:

$$d_1 + d_2 = Q(\underline{p}_o - \underline{q}_o, \underline{p}_o - \underline{q}_o) = a \quad . \tag{4.10}$$

Let $\tilde{d}_1 > d_1$, then

$$d_2 = a - d_1 > a - \tilde{d}_1 = \tilde{d}_2 \quad .$$

Thus, an upper bound to the direct problem, $\tilde{d}_1$, leads to a lower bound to the reciprocal problem, $\tilde{d}_2$.

Instead of exploring the many other cases discussed by Synge in his book [8], we will consider a quantum mechanical application of the present formulation.

4.2. Inhomogeneous Equations in Rayleigh-Schrödinger Perturbation Theory

It is very well-known that the different orders in RS perturbation theory are defined by a series of inhomogeneous equations. See PTIX, and reference 6.

$$(H_o - E_o)\psi_{n+1} = \sum_{k=0}^{n} \epsilon_{n+1-k}\psi_k - V\psi_n, \quad n=0,1,\ldots \tag{4.11}$$

$$\epsilon_{k+1} = \langle \psi_o | V | \psi_k \rangle$$

with

$$E = E_o + \sum_{k=1}^{\infty} \epsilon_k$$

$$\Psi = \sum_{k=0}^{\infty} \psi_k \tag{4.12}$$

where we have split the Hamiltonian H into an unperturbed part, H_o, and a perturbation V. Further we assume $H_o\psi_o = E_o\psi_o$.

Solutions of the "low orders" in Eq. (4.11) and Eq. (4.12) have been obtained in several problems of interest by the Wisconsin group[65]. One very important property is the result originally due to Wigner[50], if we know the approximate wave function through order n, the energy can be computed through order 2n+1.

Let us consider the first equation in Eq. (4.11), and assume that we deal with the ground state energy

$$(H_o - E_o)\psi_1 = -(V - \epsilon_1)\psi_o \tag{4.13}$$

where the first order energy is given by

$$\epsilon_1 = \langle \psi_o | V | \psi_o \rangle = V_{oo} \quad . \tag{4.14a}$$

The second order energy is

$$\epsilon_2 = \langle \psi_o | V | \psi_1 \rangle \quad . \tag{4.14b}$$

We choose ψ_1 orthogonal to ψ_o, to satisfy an intermediate normalization condition. We can construct a variational principle for Eq. (4.14) if we notice that $H_o - E_o \geq 0$, i.e., is a positive operator. Hence it can be considered as defining a positive metric in a space $\mathcal{A}$. In fact, let us identify the vectors $\underline{p}$ with functions $\tilde{\psi}$; let $\underline{p}_o = \psi_o$ and $\underline{q}_o = \psi_1$.

The direct Problem I, of Eq. (4.4) now reads:

$$d_1(\tilde{\psi}) = Q(\tilde{\psi}-\psi_1, \tilde{\psi}-\psi_1) \quad . \tag{4.15}$$

The minimum will be attained by $\tilde{\psi} = \psi_1$, the solution of Eq. (4.13). What will be d_1, the minimum of $d_1(\tilde{\psi})$?

This is seen by writing Eq. (4.15) explicitly::

$$\begin{aligned} d_1(\tilde{\psi}) &= \langle \tilde{\psi}-\psi_1 | H_o - E_o | \tilde{\psi}-\psi_1 \rangle \\ &= \langle \tilde{\psi} | H_o - E_o | \tilde{\psi} \rangle + 2\langle \tilde{\psi} | H_o - \epsilon_1 | \psi_o \rangle - \epsilon_2 \end{aligned} \tag{4.16}$$

where we have used the Hermitian property of H_o, and Eq. (4.13). The minimum, attained by $\tilde{\psi} = \psi_1$, is 0, as it can be seen by further use of Eq. (4.13). We have then:

$$\epsilon_2 \leq \langle \tilde{\psi} | H_o - E_o | \tilde{\psi} \rangle + 2\langle \tilde{\psi} | V - \epsilon_1 | \psi_o \rangle \tag{4.17}$$

This is nothing but the variational principle for the ground state second order energy due to Hylleraas[59], but derived within the geometric formulation of Synge.

This would not be of much interest if it were not for the reciprocal problem.

Let $\underline{q} = \emptyset$. Then Eq. (4.5) reads:

$$d_2(\emptyset) = Q(\emptyset-\psi_o,\emptyset-\psi_o) = Q(\emptyset,\emptyset) = \langle\emptyset|H_o-E_o|\emptyset\rangle \tag{4.18}$$

with the constraint $\emptyset-\psi_1 \in \Sigma$. The constraint amounts to impose $Q(\emptyset-\psi_1,\tilde{\psi})$ for all $\tilde{\psi}$. This would amount to restrict $\emptyset$ to be equal to ψ_1, but in fact we have more freedom than that. Consider first Eq. (4.18). The minimum is given by

$$\begin{aligned} d_1 + d_2 &= Q(\psi_o-\psi_1,\psi_o-\psi_1) = Q(\psi_1,\psi_1) \\ &= \langle\psi_1|H_o-E_o|\psi_1\rangle = -\langle\psi_1|H_1-\epsilon_1|\psi_o\rangle = -\epsilon_2 \end{aligned} \tag{4.19}$$

Then

$$d_2 = -\epsilon_2$$

and

$$\epsilon_2 \geq -d_2(\emptyset) \quad .$$

Therefore, if we could implement Eq. (4.18), we would have:

$$-d_2(\emptyset) \leq \epsilon_2 \leq d_1(\tilde{\psi}) \quad . \tag{4.20}$$

The Dalgarno-Lewis[6] procedure to determine solutions to inhomogeneous equations of the type in Eq. (4.13) can be applied in this case.

Let $\emptyset$ be written as $\emptyset = f\psi_o$. Then we have,

$$(H_o - E_o)\emptyset = (K+V-E_o)f\psi_o \tag{4.21}$$

where we have set $H_o = K + V$; K is the kinetic energy operator, which we are going to represent symbolically by a 3N-dimensional Laplacian: $K = -\frac{1}{2}\nabla^2$. V is the potential energy in the unperturbed Hamiltonian and we will assume it is a function of the coordinates of the N particles.

As shown by Hirschfelder[66], we can rewrite Eq. (4.21) by subtracting the expression $f(H_o - E_o)\psi_o$ from both sides:

$$\begin{aligned}(H_o - E_o)\emptyset &= (K+V-E_o)f\psi_o - f(K+V-E_o)\psi_o \\ &= [K,f]\psi_o = \tfrac{1}{2}[\nabla^2, f]\psi_o .\end{aligned}$$

The square brackets denote a commutator. Furthermore, we can write

$$\begin{aligned}\emptyset(H_o - E_o)\emptyset &= -\tfrac{1}{2}f\psi_o[\nabla^2, f]\psi_o \\ &= -\tfrac{1}{2}f\vec{\nabla}\cdot(\psi_o^2\nabla f) \quad . \end{aligned} \tag{4.22}$$

This follows by standard vector analysis:

$$\begin{aligned}\psi_o[\nabla^2, f]\psi_o &= \psi_o\nabla^2(f\psi_o) - \psi_o f\nabla^2\psi_o \\ &= \psi_o\vec{\nabla}\cdot\vec{\nabla}(f\psi_o) - \psi_o f\nabla^2\psi_o = \psi_o\vec{\nabla}\cdot(f\vec{\nabla}\psi_o + \psi_o\vec{\nabla}f) - \psi_o f\nabla^2\psi_o \\ &= 2\psi_o\vec{\nabla}f\cdot\vec{\nabla}\psi_o + \psi_o^2\nabla^2 f = \nabla\cdot(\psi_o^2\vec{\nabla}f) \quad .\end{aligned}$$

Therefore Eq. (4.18) is transformed into:

$$\begin{aligned}d_2(\emptyset) = d_2(f) &= -\frac{1}{2}\int f\vec{\nabla}\cdot(\psi_o^2\vec{\nabla}f)(dv) \\ &= \frac{1}{2}\int\psi_o^2\vec{\nabla}f\cdot\vec{\nabla}f(dv) - \frac{1}{2}\int\vec{\nabla}\cdot(\psi_o^2 f\vec{\nabla}f)(dv) \quad .\end{aligned}$$

The divergence term vanishes if we impose suitable boundary conditions on ϕ. This means that Eq. (4.18) can be replaced by:

$$d_2(\vec{q}) = \frac{1}{2}\int \psi_o^2 \vec{q}\cdot\vec{q}(dv) \tag{4.23}$$

where $\vec{q}$ is a vector function that satisfies an equation derivable from the inhomogeneous Eq. (4.13). Let $\phi = \Psi_1 = f\psi_o$.

$$(H_o - E_o)f\psi_o = -(V-\epsilon_1)\psi_o \quad .$$

By the same arguments as before:

$$[\nabla^2, f]\psi_o = 2(V-\epsilon_1)\psi_o$$

or

$$\nabla\cdot(\psi_o^2\vec{\nabla}f) = 2\psi_o(V-\epsilon_1)\psi_o \quad .$$

Let $\vec{\nabla}f = \vec{q}$. Then if $\vec{q}$ satisfies:

$$\nabla\cdot(\psi_o^2\vec{q}) = 2\psi_o(V-\epsilon_1)\psi_o \tag{4.24}$$

then,

$$d_2(\vec{q}) = \frac{1}{2}\int \psi_o^2\vec{q}\cdot\vec{q}(dv) \tag{4.25}$$

gives a lower bound to ϵ_2:

$$-d_2(\vec{q}) \leq \epsilon_2 \leq d_1(\tilde{\psi}) \quad . \tag{4.26}$$

In fact we have shown through a first integration of the inhomogeneous equation that it is possible to formulate the reciprocal problem and hence get a lower bound formula. It is clear that an admissible trial vector for Problem II has to satisfy Eq. (4.24), and this is by no means easy to do in general. Hirschfelder and Prager used it for the case of the polarizability of atomic hydrogen with very good results as compared with other approxinate methods. Its applicability in the future dependes then in solving Eq. (4.25) for

complicated potentials V. The extensions to higher even orders have been given by Sando and Hirschfelder[62].

Our interest is rather in studying the forcefulness of this geometric approach, and we can consider the direct problem again, within the context of perturbation theory, but for the excited states. The pertinent inhomogeneous equation is Eq. (4.13) again, but modified as follows:

$$(H_o - E_o^{(n)})\psi_1^{(n)} = -(V - \mathcal{E}_1^{(n)})\psi_o^{(n)} \quad . \tag{4.27}$$

In order to construct an upper bound to the second order energy $\mathcal{E}_2^{(n)}$, we have to insure that the metric defined by the kernel $(H_o - E_o^{(n)})$ is positive. This is achieved by restricting the space of trial functions $\psi^{(n)}$ to be orthogonal to the $\psi_o^{(k)}$, k=0,1,...,n-1, i.e., to the lower unperturbed eigenfunctions. Under this conditions, the direct Problem I applies and the extension of the Hylleraas principle to the R-S excited state second order energy follows trivially, thus proving the Sinanoğlu results: $\psi_n = \sum_{k=o}^{n-1} [V_{kn}/(E_o^{(n)} - E_o^{(k)})]\psi_o^{(k)} + \psi^{(n)}$.

This shows that the initial care in introducing the geometric approach has the consequence of providing unified and simple derivations of the lower and upper bound formulae in R-S theory. It is certainly of great interest to extend it to other problems, and by no means, this has been done to any extent.

4.3. Inhomogeneous Equations in Brillouin-Wigner Perturbation Theory

There is an entirely analogous derivation for upper bounds to the B-W even order energies. In this case, for $\mathcal{E} < E_1^o$, the operator

$H_o - \mathcal{E}$ is positive definite in the orthogonal complement to ψ_o, and the subspace of $\underline{p}$ vectors, i.e., the $\tilde{\psi}$ functions are to be chosen orthogonal to ψ_o.

Consider the inhomogeneous equation for the ground state first order wave function in the B-W scheme

$$(H_o - \mathcal{E})\psi_1 + (V - \epsilon_1)\psi_o = 0 \quad . \tag{4.28}$$

The second order energy is defined by

$$\epsilon_2 = \langle \psi_o | V | \psi_1 \rangle \quad . \tag{4.29}$$

As before, let $\underline{p} = \tilde{\psi}$, $\underline{p}_o = \psi_o$, and $\underline{q}_o = \psi_1$. The direct problem in Eq. (4.4) yields:

$$\begin{aligned} d_1(\tilde{\psi}) &= Q(\tilde{\psi} - \psi_1, \tilde{\psi} - \psi_1) = \langle \tilde{\psi} - \psi_1 | H_o - \mathcal{E} | \tilde{\psi} - \psi_1 \rangle \\ &= \langle \tilde{\psi} | H_o - \mathcal{E} | \tilde{\psi} \rangle - 2\langle \tilde{\psi} | H_o - \mathcal{E} | \psi_1 \rangle + \langle \psi_1 | H_o - \mathcal{E} | \psi_1 \rangle \quad . \end{aligned}$$

By use of Eq. (4.28):

$$\begin{aligned} d_1(\tilde{\psi}) &= \langle \tilde{\psi} | H_o - \mathcal{E} | \tilde{\psi} \rangle + 2\langle \tilde{\psi} | V - \epsilon_1 | \psi_o \rangle - \langle \psi_1 | V - \epsilon_1 | \psi_o \rangle \\ &= \langle \tilde{\psi} | H_o - \mathcal{E} | \tilde{\psi} \rangle + 2\langle \tilde{\psi} | V | \psi_o \rangle - \epsilon_2 \quad . \end{aligned} \tag{4.30}$$

The minimum of $d_1(\tilde{\psi})$ is $d_1 = 0$, for $\tilde{\psi} = \psi_1$. Therefore,

$$\epsilon_2 = \langle \tilde{\psi} | H_o - \mathcal{E} | \tilde{\psi} \rangle + 2\langle \tilde{\psi} | V | \psi_o \rangle \tag{4.31}$$

for all $\tilde{\psi}$ orthogonal to ψ_o, and this is the desired variational principle, whose generalizations to higher orders and to excited states follow the same lines as the previous section. On the other hand, the reciprocal problem cannot be implemented in a simple fashion, because a first integration, by quadratures, of the B-W equations is not available[67].

CHAPTER V

PARTITIONING TECHNIQUE AND THE METHOD OF INTERMEDIATE PROBLEMS

In Chapter III we have discussed a truncation of T_o, denoted by $T'_o(p)$. We did not discuss at all the truncation $T_o(p)$, which for our purposes in obtaining lower bounds is far more reaching. We'll relate it to the method of intermediate problems and point out some of the limitations of the latter. Finally, we'll give some by-products of the partitioning approach to the intermediate Hamiltonians, like lower bounds to the $\overline{E}_i$'s and improved energy estimates.

5.1. The Truncation $T_o(p)$

We will start with a single reference function, an eigenfunction to H_o, the unperturbed Hamiltonian. Then the following formulae are valid, as shown in Chapter I:

$$H_o \psi_k^o = E_k^o \psi_k^o \tag{5.1}$$

$$H\psi_k = E_k \psi_k \tag{5.2}$$

$$\mathcal{E}_{1,k} = E_k^o + \langle \psi_k^o | t | \psi_k^o \rangle \tag{5.3}$$

$$t = (V^{-1} - T_o)^{-1} \tag{5.4}$$

$$T_o \equiv \sum_{\ell \neq k}^{\infty} \frac{O_\ell^o}{\mathcal{E} - E_\ell^o} \tag{5.5}$$

and if $E_k < \mathcal{E}$, $\mathcal{E}_{1,k} < E_k$ follows.

Assume that $\mathcal{E} < E^o_{p+1}$. Then, from Eq. (1.30):

$$T_o \equiv \sum_{\ell \neq k}^{p} \frac{O^o_\ell}{\mathcal{E} - E^o_\ell} + \sum_{\ell=p+1}^{\infty} \frac{O^o_\ell}{\mathcal{E} - E^o_\ell} \geq \sum_{\ell \neq k}^{p} \frac{O^o_\ell}{\mathcal{E} - E^o_\ell} + \frac{1}{\mathcal{E} - E^o_{p+1}} \sum_{\ell=p+1}^{\infty} O^o_\ell$$

$$= \sum_{\ell \neq k}^{p} \frac{O^o}{\mathcal{E} - E^o_\ell} + \frac{1}{\mathcal{E} - E^o_{p+1}} \left\{ 1 - \sum_{\ell=o}^{p} O^o_\ell \right\} \equiv T_o(p) \quad . \tag{5.6}$$

Let's assume that $\mathcal{E} < E^o_1$ and that we consider the ground state. Then $0 \geq T_o \geq T_o(p)$. For positive V, $V^{-1} > 0$ and

$$0 < V^{-1} - T_o \equiv t^{-1} \leq V^{-1} - T_o(p) \equiv t^{-1}(p) \quad . \tag{5.7}$$

According to theorem 1.6, it follows that

$$0 < t(p) < t \tag{5.8}$$

and Eq. (5.3) may be replaced by

$$\mathcal{E}^1_1 = E^o_o + \langle \psi_o | [V^{-1} - T_o(p)]^{-1} | \psi_o \rangle \tag{5.9}$$

where we have a bracketing of the ground state eigenvalue:

$$\mathcal{E}^1_1 < E_o < \mathcal{E} \quad . \tag{5.10}$$

It is interesting to see that there is no need to expand the inverse in Eq. (5.9) in a power series to obtain a Brillouin-Wigner solution. We can solve Eq. (5.9) to all orders by introducing an inhomogeneous equation approach entirely similar to what was done in Chapter III. Let X be a function defined by

$$[V^{-1} - T_o(p)]^{-1} \psi_o = X$$

or

$$[V^{-1}-T_o(p)]X = \psi_o \ . \tag{5.11}$$

We just have to replace Eq. (5.6) into Eq. (5.11) and perform some algebraic transformations:

$$\psi_o = [V^{-1}-(\mathcal{E} - E^o_{p+1})^{-1}]X$$

$$+ \sum_{\ell=o}^{p} \psi^o_\ell[(\mathcal{E} - E^o_{p+1})^{-1}-(\mathcal{E} - E^o_\ell)^{-1}(1-\delta_{o\ell})]\langle\psi^o_\ell|X\rangle \ .$$

We can multiply by $\psi^o_k[V^{-1}-(\mathcal{E} - E^o_{p+1})^{-1}]^{-1} \equiv \psi^o_k v$, and integrate, thus obtaining

$$\langle\psi^o_k|v|\psi^o_o\rangle$$

$$= \langle\psi^o_k|X\rangle + \sum_{\ell=o}^{p} \langle\psi^o_k|v|\psi^o_\ell\rangle[(\mathcal{E} - E^o_{p+1})^{-1} - (\mathcal{E} - E^o_\ell)^{-1}(1-\delta_{o\ell})]\langle\psi^o_\ell|X\rangle \ .$$

Let us denote $\langle\psi^o_k|v|\psi^o_\ell\rangle$ by $v_{k\ell}$, $\langle\psi^o_\ell|X\rangle$ by C_ℓ, and $[(\mathcal{E} - E^o_{p+1})^{-1} - (\mathcal{E} - E^o_\ell)^{-1}(1-\delta_{o\ell})]$ by d_ℓ. Then Eq. (5.11) is finally transformed into the system of equations:

$$v_{ko} = C_k + \sum_{\ell=o}^{p} v_{k\ell}\ d_\ell\ C_\ell, \quad \ell,k = o,1,\ldots,p. \tag{5.12}$$

We can express Eq. (5.12) in more compact form by using matrix notation. Let $\mathbb{v}_o$ be a column vector with the v_{ko}'s as components; let $\mathbb{C}$ be a column vector with the C_k's as components and let $\mathbb{A}$ be a square

matrix, with $(\mathbb{A})_{k\ell} = v_{k\ell} d_\ell$. Then Eq. (5.12) can be written:

$$\mathbb{v}_o = \mathbb{C} + \mathbb{A}\mathbb{C} = (1+\mathbb{A})\mathbb{C} \quad . \tag{5.13a}$$

This means then:

$$\mathbb{C} = (1+\mathbb{A})^{-1}\mathbb{v}_o \ , \tag{5.13b}$$

and

$$\langle \psi_o^o | X \rangle \equiv [(1+A)^{-1}\mathbb{v}_o]_o = \sum_{\ell=o}^{p} [(1+\mathbb{A})^{-1}]_{o\ell} v_{\ell o} \tag{5.14}$$

is the explicit form of $\langle \psi_o^o | t(p) | \psi_o^o \rangle$. It should be pointed out that the inverse matrix in Eqs. (5.13) and (5.14) does not have to be computed, because all we need is the solution of the system of Eq. (5.12). The discussion of the solution of this system of equations parallels the discussion of the system of equations that arose in Chapter III and led to Feenberg's perturbation theory. The coefficients are slightly different and there are new integrals, the

$$v_{k\ell} = \langle \psi_k^o | [V^{-1} - (\mathcal{E} - E_{p+1}^o)^{-1}]^{-1} | \psi_\ell^o \rangle \tag{5.15}$$

to be evaluated. The compensation of this additional complication is that for $\mathcal{E} < E_1^o$ we obtain a lower bound to the ground state energy. The fact that Eq. (5.9) itself is a bracketing function, i.e., it has negative slope, suggests the examination of the point $\mathcal{E}_1^1 = \mathcal{E} = E_o^1$. It is quite clear that E' is bracketed by the pair $\mathcal{E}_1^1, \mathcal{E}$; but this does not imply a simultaneous bracketing of E_o. Is E_o^1 a lower bound to E_o? The answer to this is yes, and it is given by the theory of intermediate problems, as we will see in the next section.

Could we apply the same treatment to excited states? It is easy to see that a system of equations entirely similar to Eq. (5.12) could be obtained, but we have not proved that Eq. (5.8) applies. In fact we will see that Eq. (5.8) is too strong a condition and that it will have to be modified. So, even though we have not proved that $\langle\psi_k^o|t(p)|\psi_k^o\rangle$ is smaller than $\langle\psi_k^o|t|\psi_k^o\rangle$, we will get an explicit form for it: it is just a modification of the system of Eq. (5.12):

$$v_{mk} = C_{mk} + \sum_{\ell=o}^{p} v_{m\ell} d_\ell(k) C_{\ell k} \ , \quad (\ell,m,k=o,1,\ldots,p) \tag{5.16}$$

where we defined $C_{mk} = \langle\psi_m^o|X_k\rangle$

and $d_\ell(k) = [(\mathcal{E} - E_{p+1}^o)^{-1} - (\mathcal{E} - E_\ell^o)^{-1}(1-\delta_{k\ell})]$;

the v_{mk}'s are the same as in Eq. (5.15).

The solution of this system of equations leads to an explicit form for Eq. (5.3):

$$\mathcal{E}_{1,k}^1 = E_k^o + C_{kk}. \tag{5.17}$$

In Eq. (5.17) we can impose the condition $\mathcal{E}_{1,k} = \mathcal{E} = E_k^t$. In Chapter III, we showed that this condition led to a secular equation. It can be shown that the same is true, and we examine this question in the next section; the only point we want to emphasize here is that the truncation $T_o(p)$ implies that there is no need for a power series expansion of the inverse operator $[V^{-1}-T_o(p)]^{-1}$ in order to compute its matrix elements, thus avoiding the convergence and further truncations of the BW series.

5.2. Intermediate Problems

The method of intermediate problems was developed by the Weinstein, Aronszajn school [3]. In particular Bazley and Fox made extensive contributions to it, within the context of quantum mechanical applications [34]. In terms of the theorems introduced in Chapter I it is simple to define a sequence of intermediate problems corresponding to a specific eigenvalue problem. Let A be a self-adjoint operator bounded from below. Then

$$Au_k = a_k u_k \tag{5.18}$$

is the eigenvalue problem under consideration. Suppose that we can construct a series of operators $A^{(p)}$ that satisfy:

$$A^{(o)} \leq A^{(1)} \leq \ldots \leq A^{(p)} \leq A^{(p+1)} \leq \ldots A \quad . \tag{5.19}$$

For each of them there is an eigenvalue problem

$$A^{(p)} u_k^{(p)} = a_k^{(p)} u_k^{(p)} \quad . \tag{5.20}$$

Then theorem (1.2) states that

$$a_k^{(o)} \leq \ldots \leq a_k^{(p)} \leq a_k^{(p+1)} \leq \ldots \leq a_k, \text{ in order} \quad . \tag{5.21}$$

Thus, to obtain lower bounds to the eigenvalues of Eq. (5.18) we need the requirements: we should be able to construct the operators $A^{(p)}$; they should be solvable, and we should keep track of the ordering Eq. (5.21). The last requirement is important in connection with lost eigenvalues. As the k^{th} eigenvalue of $A^{(p)}$ is a lower bound to the k^{th} eigenvalue of A, it is important to make sure that all the

eigenvalues of $A^{(p)}$ are obtained, otherwise the ordering can not be implemented.

If $A = A_o + B$, where A_o has a known spectral resolution, we can define a series of truncations $A_o^{(p)}$:

$$A_o^{(p)} = \sum_{k=o}^{p} a_k^o O_k^o + a_{p+1}^o (1 - \sum_{k=o}^{p} O_k^o) \tag{5.22}$$

where $O_k^o = |u_k^o\rangle\langle u_k^o|$; $A_o u_k^o = a_k^o u_k^o$.

If A_o is bounded from below, and $a_o^o \leq a_1^o \leq \ldots \leq a_p^o \leq a_{p+1}^o \leq \ldots$, it follows that

$$A_o^{(o)} \leq A_o^{(1)} \leq \ldots \leq A_o^{(p)} \leq A_o^{(p+1)} \leq \ldots \leq A_o \quad . \tag{5.23}$$

Then we can define a sequence of operators $A^{(p)} = A_o^{(p)} + B$ which satisfies the relations:

$$A^{(o)} \leq A^{(1)} \leq \ldots \leq A^{(p)} \leq A^{(p+1)} \leq \ldots \leq A \quad . \tag{5.24}$$

This means that if we can solve the eigenvalue problem for $A^{(p)}$, a set of lower bounds to the eigenvalues of Eq. (5.18) is obtained. This, so far, does not require B to be positive definite. But if the eigenvalue problem corresponding to the $A^{(p)}$'s is not solvable or not easily solvable, in the case of B positive definite, a new sequence may be defined

$$A'^{(o)} \leq A'^{(1)} \leq \ldots \leq A'^{(p)} \leq A'^{(p+1)} \leq \ldots A \tag{5.25}$$

where

$$A'^{(i)} = A_o^{(i)} + B^{\frac{1}{2}} O B^{\frac{1}{2}} = A_o^{(i)} + B' \quad . \tag{5.26}$$

By theorem 1.9 $B' \triangleq B$ and then Eq. (5.25) follows. The important thing in this connection is that the inner projection is entirely arbitrary. Consider for instance the Bazley projection defined in Eq. (1.57):

$$B' = |\Omega\rangle\langle\Omega|B^{-1}|\Omega\rangle\langle\Omega| \quad . \tag{5.27}$$

The operator $A^{(p)}$ is now:

$$A^{(p)} \triangleq \sum_{k=o}^{p} a_k^o |u_k^o\rangle\langle u_k^o| + a_{p+1}^o (1 - \sum_{k=o}^{p} |u_k^o\rangle\langle u_k^o|) + |\Omega\rangle\langle\Omega| B^{-1} |\Omega\rangle\langle\Omega| \quad . \tag{5.28}$$

The solutions of $A^{(p)} u_k^{(p)} = a_k^{(p)} u_k^{(p)}$ will be spanned by the functions u_k^o, $k = o, \ldots, p$ and by the linear manifold Ω. We may choose it to consist precisely of the same functions u_k^o. Then as Bazley and Fox have shown[34], the solutions may be shown by solving a secular problem. In fact, the common feature of the intermediate problems is that they lead to a finite secular equation for the lower bounds.[68,69].

We want to emphasize that partitioning technique can give explicit solutions to the secular equations of the intermediate problems, the only requirement being that equivalent truncations are made for $A^{(p)}$ or $A'^{(p)}$ and the appropriate reduced resolvents. Consider for instance, Miller's[70] work on the excited states of He. He applied Bazley's Eq. (5.23) to H_o. More explicitly, given $H_o + V$ for the He atom, where V is just r_{12}^{-1}, the spectral resolution of H_o is known. The truncation $H_o^{(p)}$ leads then to a secular equation. Instead of deriving the secular equation in the same way as Miller, we point out that the truncation $T_o(p)$ is just the inverse of $H_o^{(p)}$ in the

orthogonal complement to ψ_k^o. Therefore it follows that the solution of Eq. (5.17), given by the system of Eq. (5.16), for $\mathcal{E}_{1k} = \mathcal{E}$ should coincide with one of the roots of Miller's secular equation, just because $P(\mathcal{E} - H_o^{(p)})T_o(p) = P$. Equation (5.16) is one solution of $H_o^{(p)} + V$, when $\mathcal{E}_{1,k} = \mathcal{E}$. We can verify this explicitly, and this constitutes an alternate proof. Of course the proof is similar to the transformation done in Chapter III.

Consider Eq. (5.16). If we replace $d_\ell(k)$ by d_ℓ, defined by

$$d_\ell = [(\mathcal{E} - E_{p+1}^o)^{-1} - (\mathcal{E} - E_\ell^o)^{-1}] = \frac{E_{p+1}^o - E_\ell^o}{(\mathcal{E} - E_{p+1}^o)(\mathcal{E} - E_\ell^o)} \quad . \tag{5.29}$$

The only term that changes in Eq. (5.15) is the k^{th} term in the summation:

$$v_{mk} d_k(k) C_{kk} = v_{mk} d_k C_{kk} + v_{mk}(\mathcal{E} - E_k^o)^{-1} C_{kk} \quad .$$

But if we impose $\mathcal{E}' - E_k^o = C_{kk}$, Eq. (5.16) may be written:

$$0 = \sum_{\ell=o}^{p} (v_{m\ell} d_\ell + \delta_{m\ell}) C_{\ell k} \quad . \tag{5.30}$$

The condition for existence of a non-trivial solution is

$$|v_{m\ell} d_\ell + \delta_{m\ell}| = 0 \quad . \tag{5.31}$$

Note that:

$$\begin{aligned} v_{m\ell} &= \langle \psi_m^o | \frac{V(\mathcal{E} - E_{p+1}^o)}{\mathcal{E} - E_{p+1}^o - V} | \psi_\ell^o \rangle \\ &= -(\mathcal{E} - E_{p+1}^o)\delta_{m\ell} - \langle \psi_m^o | (E_{p+1}^o - \mathcal{E} + V)^{-1} | \psi_\ell^o \rangle \quad . \end{aligned} \tag{5.32}$$

Then Eq. (5.31) can be written in the following way:

$$\left| \delta_{m\ell}\left(1 - \frac{E^o_{p+1} - E^o_\ell}{\mathcal{E}' - E^o_\ell}\right) - \langle \psi^o_m | (E^o_{p+1} - \xi + V)^{-1} | \psi^o_\ell \rangle \frac{(\mathcal{E}' - E^o_{p+1})(E^o_\ell - E^o_{p+1})}{(\mathcal{E}' - E^o_{p+1})} \right| = 0.$$

If we multiply the ℓ^{th} column by $\dfrac{\mathcal{E}' - E^o_\ell}{(\mathcal{E}' - E^o_{p+1})(E^o_\ell - E^o_{p+1})}$ we obtain

$$\left| \frac{\delta_{m\ell}}{E^o_\ell - E^o_{p+1}} - \langle \psi^o_m | (E^o_{p+1} - \xi + V)^{-1} | \psi^o_\ell \rangle \right| = 0 \qquad (5.33)$$

which is indeed the secular determinant solved by Miller.

We haven't derived Eq. (5.33) because it is in any sense a better equation to work with. We wanted to establish a formal connection between the partitioning formula in Eq. (5.17) and the solutions of the intermediate problem given by Eq. (5.33). The fact is that Eq. (5.17) provides an iterative method of solution to Eq. (5.33), and any pair $(\mathcal{E}_{lk}, \mathcal{E})$ bracket at least one eigenvalue of the intermediate problem.

It would seem then that the partitioning method does not offer anything but a convenient way of solving the intermediate problem. For the ground state, provided $\mathcal{E}$ is an upper bound to E_o, the bracketing function yielded a lower bound which was worse than the ground state of the intermediate problem. For the excited states we were not able to verify Eq. (5.8), and hence it seems that the only useful information comes from the intermediate problems. The difficulty here lies in the use of a single reference function as we will see in the next section. Furthermore, the truncation of $T_o(p)$ is by no means the only way of

evaluating the bracketing function Eq. (1.50), as shown in PTX, PTXI, and in the book by Choi[71] on He-like ions.

5.3. The Bracketing Function Associated with $T_o(p)$

Consider

$$\mathcal{E}'_{1,k} = E^o_k + \langle \psi^o_k | (V^{-1} - T_o(p))^{-1} | \psi^o_k \rangle \tag{5.34}$$

with $T_o(p)$ defined in the orthogonal complement to ψ^o_k. Clearly,

$$\frac{d\mathcal{E}'_{1,k}}{d\mathcal{E}} \leq 0 \quad . \tag{5.35}$$

Then Eq. (5.34) is a bracketing function. The asymptotes of Eq. (5.34) are different from the eigenvalues of PHP, which are the asymptotes of

$$\mathcal{E}_{1,k} = E^o_k + \langle \psi^o_k | (V^{-1} - T_o)^{-1} | \psi^o_k \rangle \quad . \tag{5.36}$$

But, from the previous section we may conclude that the asymptotes of Eq. (5.34) are given by the eigenvalues of

$$PH^{(p)}P = P(H^{(p)}_o + V)P \leq PHP \quad .$$

By theorem 1.2 we have: $\bar{E}^{(p)}_k \prec \bar{E}_k$, in order. So if we use the ordering theorem, and examine under what conditions Eq. (5.34) blows up, lower bounds to the $\bar{E}_k$'s may be found.

There are two consequences of this fact. One, that these lower bounds may be used in conjunction with the Eckart-type formulae of Chapter II, and with the Temple formula, as mentioned in the discussion following Eq. (2.15).

The second consequence is in connection with the inequality $t(p) \leq t$, which holds under restricted conditions. From the preceding it follows that Eq. (5.35) holds and that the asymptotes of Eq. (5.34) are lower bounds to t for all $\mathcal{E}$. We can examine the situation in a diagram. See figure 6. It follows that there are ranges where $t(p) \geq t$. We may have several situations, and for the purpose of this discussion it is enough to consider a well behaved case, where we have

$$E_o' < E_o < \bar{E}_1' < \bar{E}_1 < E_1' < E_1 < \bar{E}_2' < \bar{E}_2 < \cdots .$$

It is clear that in the intervals $(\bar{E}_1', \bar{E}_1)$, $(\bar{E}_2', \bar{E}_2)$, $t(p)$ is larger than t instead of being a lower bound to it. But regardless of the complexity of the situation, we may find the asymptotes, and hence the eigenvalues of PH'P, which are lower bounds to the $\bar{E}_i$'s of Chapter II. Consider Eq. (5.14), the explicit formula for $\langle \psi_o^o | t(p) | \psi_o^o \rangle$. It blows up whenever $(1+\mathbb{A})^{-1}_{o\ell}$, $\ell = o, 1, \ldots, p$, blows up. Consider for simplicity the case p=o. Then it blows up for $(1+\mathbb{A})_{oo} = o$, or:

$$1 + v_{oo} d_o = 0 \tag{5.37}$$

which may be written, using Eqs. (5.32) and (5.12):

$$1 - [(\bar{\mathcal{E}} - E_1^o) - \langle \psi_o^o | (E_1^o - \bar{\mathcal{E}} + V)^{-1} | \psi_o^o \rangle] \frac{1}{\mathcal{E} - E_1^o} = 0$$

and then,

$$\langle \psi_o^o | (E_1^o - \bar{\mathcal{E}} + V)^{-1} | \psi_o^o \rangle = 0 \tag{5.38}$$

is the simplest formula that gives a lower bound to $\bar{E}_1$ within this scheme. Of course Eq. (5.14) provides a whole family of equations in $\bar{\mathcal{E}}$

that when solved, give lower bounds to the $\overline{E}_i$'s; Eq. (5.38) does not give a very good lower bound, but it may be improved by considering higher p's.

We see then that a byproduct of using the bracketing function to compute the eigenvalues of the intermediate problem is that it provides simultaneously a scheme to compute lower bounds to the eigenvalues of PHP and hence quantities useful in the estimates of the Weinstein function, as in Eqs.(1.29), (2.10), and, Temple's formula Eq. (2.9). These estimates may prove very useful in connection with the full resolvent technique(Section 1.2). The integrals appearing in the scheme have been evaluated numerically by Miller, but further research should prove interesting, especially to obtain them in closed form and study their properties.

The drawback with the intermediate problems associated with a truncation of H_o, and hence with the truncation $T_o(p)$ is that the discrete spectrum is by no means complete. To expect convergence to the exact eigenvalue one should be able to compute the full spectral resolutions. The integration over the continuum is no easy task. In the next chapter we discuss this further and make an attempt to cope with this difficulty. Far more important is the fact that the truncation $T_o(p)$ is not the only way to evaluate the bracketing function. As Löwdin showed in PTX and PTXI, the inner projection on V, or on $t_\mathcal{E}$ when by suitable conditions its possitivity is insured, yields expressions where the operator T_o has been transformed away. We refer to the substitution $\mathfrak{u} = (\mathcal{E} - H_o)\mathfrak{y}$ in Eq. (1.57). This implies the use of the linear manifold $\mathfrak{y}$, called Löwdin Space by Choi[71]. This

substitution removes the dependence on T_o, and the only requirement is one on the domains of the operators involved. Any qualms about the accuracy of this "variational" estimate of T_o are removed by the accuracy of Choi's results, and they go beyond the intermediate problems.

The multidimensional reference function, discussed in [12] and PTXI has the further flexibility of allowing a treatment without any reference to an intermediate Hamiltonian, i.e., provided that i) $\mathcal{E} < E^o_{p+1}$, ii) the reference function is a linear combination of the first p+1 eigenfunctions to H_o, iii) the Aronszajn space g, Eq. (1.56), contains at least these same functions, then there is an inner projection of $V,V' = \bar{V}^{\frac{1}{2}}QV^{\frac{1}{2}}$ associated with an operator t', which fulfills $t' < t$, and then $\mathcal{E}_1' = E_o + \langle\psi^o|t'|\psi^o\rangle$ and $\mathcal{E}$ bracket one eigenvalue of H. This is thoroughly discussed in PTXI but we mention it for completeness.

5.4. Improved Energy Estimates

The starting point is Eq. (1.14), and by use of Eq. (1.15) and Eq. (1.18) we obtain

$$E = \mathcal{E} - \epsilon = \xi - \frac{\epsilon_1}{q(E+\theta\epsilon)} = \mathcal{E} - \frac{\epsilon_1 - E}{q(E+\theta\epsilon)}$$

which may be transformed into:

$$E = \mathcal{E} - \frac{\mathcal{E} - \mathcal{E}_1}{1+q(E+\theta\ )} \qquad . \tag{5.39}$$

We shall restrict our attention to the gound state, and assume that $\mathcal{E}$ is an upper bound, in which case $\mathcal{E}_1$ is a lower bound, i.e., $\mathcal{E}_1 \leq E \leq \mathcal{E}$.

Eq. (1.17) tells us that

$$\mathcal{E}_1 \leq E \leq \mathcal{E}^* \leq \mathcal{E} \tag{5.40}$$

where

$$\mathcal{E}^* = \mathcal{E} - \frac{\mathcal{E} - \mathcal{E}_1}{1 + q(\mathcal{E})} \quad . \tag{5.41}$$

In fact Eq. (5.40) follows from Eq. (5.41) and Eq. (5.39) if we make use of theorem 1.1, as $q(E+\theta\mathcal{E}) \leq q(\mathcal{E})$.

Use of theorem 1.1 in Eq. (5.39) leads to:

$$\mathcal{E} - \frac{\mathcal{E} - \mathcal{E}_1}{1 + q(\mathcal{E}_1)} < E < \mathcal{E} - \frac{\mathcal{E} - \mathcal{E}_1}{1 + q(\mathcal{E})}$$

and for $\mathcal{E}_1' < \mathcal{E}_1$, where $\mathcal{E}_1'$ is a computable lower bound to the bracketing function:

$$\mathcal{E}_1' \leq \mathcal{E} - \frac{\mathcal{E} - \mathcal{E}_1'}{1 + q(\mathcal{E}_1')} < E < \mathcal{E} - \frac{\mathcal{E} - \mathcal{E}_1}{1 + q(\mathcal{E})} < \mathcal{E} \quad . \tag{5.42}$$

The inequalities in Eq. (5.42) are very interesting because they indicate that if we start with an upper bound $\mathcal{E}$, an improved upper bound, and an improved lower bound may be obtained provided the slopes may be evaluated at the points $\mathcal{E}$ and $\mathcal{E}_1'$. As it might be anticipated these slopes cannot, in general, be obtained exactly, yet bounds to them may be used in Eq. (5.40).

If we recall the definition of $q(\mathcal{E})$:

$$q(\mathcal{E}) = \langle \psi | H T^2 H | \psi \rangle \tag{5.43}$$

it is apparent that operator inequalities involving T^2 are the required tools on account of theorem 1.3. Equation (2.7) gives a bound for T,

provided $\mathcal{E} < \bar{E}_1$:

$$0 > T \geq \frac{P}{\mathcal{E} - \bar{E}_1} \quad .$$

As T and $\frac{P}{\mathcal{E} - \bar{E}_1}$ commute, it follows that

$$T^2 \leq \frac{P}{(\bar{E}_1 - \mathcal{E})^2} \quad . \tag{5.44}$$

Alternatively, Eq. (5.44) may be derived from the spectral resolution of T^2. Substituting into Eq. (5.43):

$$q(\mathcal{E}) \leq \frac{\langle\psi|HPH|\psi\rangle}{(\bar{E}_1 - \mathcal{E})^2} = \frac{(\Delta H)^2}{(\bar{E}_1 - \mathcal{E})^2} \quad . \tag{5.45}$$

This is a very interesting relation, because it gives a bound to the slope of the bracketing function in terms of the mean square deviation of the Hamiltonian with respect to the bracketing function and of the first eigenvalue of PHP.

Lower bounds to $\bar{E}_1$ may be replaced into Eq. (5.45) without violating the inequality, and we have then:

$$q(\mathcal{E}) \leq \frac{(\Delta H)^2}{(\bar{E}_1' - \mathcal{E})^2} \quad . \tag{5.46}$$

Thus we see a further application of the lower bounds to $\bar{E}_1$ that were suggested in the previous section. Substitution of Eq. (5.45) in Eq. (5.42) yields:

$$E < \mathcal{E} - \frac{\mathcal{E} - \mathcal{E}_1}{1 + (\Delta H)^2/(\bar{E}_1 - \mathcal{E})^2} \quad . \tag{5.47}$$

If instead of providing lower bounds to $\bar{E}_1$, we set

$$\bar{E}_1 - \mathcal{E} = E_1 - \langle H \rangle ,$$

in the same way as when we derived Temple's formula in Eq. (2.6) from Eq. (2.9), we obtain

$$E < \langle H \rangle - \frac{\langle H \rangle - \mathcal{E}_1}{1 + (\Delta H)^2/(E_1 - \langle H \rangle)^2} < \langle H \rangle \quad . \tag{5.48}$$

A possible line of development here is to replace an estimate of $\mathcal{E}_1$ in Eq. (5.48). Strictly speaking we need an upper bound to $\mathcal{E}_1$ which is smaller than E. As this is not available, we replace a lower bound thus obtaining an approximate energy, not necessarily an upper or a lower bound, but within the interval bracketing the energy. For instance, use the Temple bound, E_T, for $\mathcal{E}_1$ in Eq. (5.48). Then:

$$\begin{aligned} E &\simeq \langle H \rangle - \frac{\langle H \rangle - \langle H \rangle + (\Delta H)^2/(E_1 - \langle H \rangle)}{1 + (\Delta H)^2/(E_1 - \langle H \rangle)^2} \\ &\simeq \langle H \rangle - \frac{(\Delta H)^2}{E_1 - \langle H \rangle + (\Delta H)^2/(E_1 - \langle H \rangle)} \equiv \tilde{E} \quad . \end{aligned} \tag{5.49}$$

We have then:

$$E_T < \tilde{E} < \langle H \rangle, \quad \text{and} \quad E_T < E < \langle H \rangle \quad . \tag{5.50}$$

$\tilde{E}$ is smaller than the average of E_T and $\langle H \rangle$ provided that

$$(E_1 - \langle H \rangle)^2 > (\Delta H)^2 \quad .$$

Equation (5.49) does not seem very interesting because, for reasonably accurate wave functions, $(\Delta H)^2$ is small and E should be slightly bigger

than the Temple bound E_T. Therefore we may expect that the $\ell\cdot h\cdot s\cdot$ of Eq. (5.42) should enable us to obtain more insight. Let $\mathcal{E}_1'$ be any computed lower bound to the bracketing function:

$$\mathcal{E}_1' \leq \mathcal{E} - \frac{\mathcal{E} - \mathcal{E}_1'}{1 + q(\mathcal{E}_1')} < E < \mathcal{E}. \tag{5.51}$$

In order to apply Eq. (5.51) we need a lower bound to q_1, different from the trivial one, equal to zero. Here we may appeal to the inner projection concept. By theorem 1.9, as $T^2 \geq 0$.

$$T^2 > (-T)Q(-T) > 0,$$

where Q is a projection operator. Hence, by theorem 1.3 we have

$$HT^2H > H(-T)Q(-T)H > 0.$$

Choose $Q = \bar{O}_1$, the first projector in the spectral resolution of (-T). Then we have:

$$HT^2H > \frac{H\bar{O}_1H}{(\bar{E}_1 - \mathcal{E})^2} \quad . \tag{5.52}$$

We may derive an Eckart-type theorem for $\bar{O}_1$:

$$PHP - \bar{E}_1P = \sum_{k=2} (E_K - E_1)\bar{O}_K \geq (\bar{E}_2 - \bar{E}_1)(P - \bar{O}_1) > 0 \quad .$$

Then,

$$\frac{PHP - \bar{E}_1P}{\bar{E}_2 - \bar{E}_1} \geq P - \bar{O}_1$$

or

$$\bar{O}_1 > \frac{P(\bar{E}_1 - H)P}{\bar{E}_2 - \bar{E}_1} \quad . \tag{5.53}$$

Replacing Eq. (5.53) in Eq. (5.52) we obtain for $q(\varepsilon)$:

$$q(\varepsilon) > \frac{\langle\psi|\, HP(\overline{E}_2-H)PH\,|\psi\rangle}{(\overline{E}_2-\overline{E}_1)(\overline{E}_1-\varepsilon)^2} \quad . \tag{5.54}$$

Equation (5.54) should be studied in conjunction with Eq. (5.51).

We see that estimates of the eigenvalues of PHP appear as well as the expectation value of H^3, which seems a rather gloomy perspective but for reference functions constructed in terms of eigenfunctions of H_o the questions of operator domains may be coped with. This seems to indicate that the energy estimates and improved bounds through computation of derivatives of the bracketing function offer possibilities of development and application.

CHAPTER VI

AN EIGENVALUE TRANSFORMATION

In the preceding chapters we have studied some aspects of partitioning technique and the calculation of upper and lower bounds to eigenvalues. An all pervading feature was the need for a splitting of the Hamiltonian into an unperturbed part, H_o, and a perturbation, V. The spectrum of the unperturbed Hamiltonian or at least its lower part, i.e., the first eigenvalues and eigenfunctions had to be known, in order to construct a tractable reference function. The spectrum is not actually needed to compute the reduced resolvent T_o if one carries the transformation to the Löwdin space, as in PTX and in reference [71]. Of course, the first part of the spectrum is needed in the method of truncations. At any rate, the need for an H_o with a partially discrete and known spectrum is not necessarily compatible with a positive V prerequisite for inner projections and all the transformations employed previously.

In atoms it is natural to split the Hamiltonian into an unperturbed part with the desired characteristics and a perturbation V, which is positive definite. In molecules, if one considers an unperturbed part for which the lower part of the spectrum is known, the perturbation is not positive. If one chooses the perturbation in the same way as in atoms, i.e., the interelectronic repulsion, the unperturbed spectrum has no known spectrum. This dilemma was faced by

Bazley and Fox[72], who suggested a method of truncations combined with a splitting of the unperturbed Hamiltonian into parts corresponding to the different nuclei. Johnson and Coulson[73] carried out a calculation for H_2^+ with this scheme, and the results were not very good, the reason being that the truncations involved threw away the significant continuum contribution.

The question is then, is it possible to transform the original Schrödinger equation in such a way that one has a complete discrete spectrum? Is this in any way related to the possibility of splitting the Hamiltonian into two parts, one of which is positive leaving a tractable H_o? The answer to the first problem is partially affirmative. For one electron problems, it is possible to do an eigenvalue transformation that yields a complete, discrete spectrum. This was known to Schrödinger[74] and to others.[75] Lundqvist[76] discussed the problem in terms of a Green's function approach and mentioned that for many electron problems the solutions should be interesting, because, for the unperturbed problem, each "state" is described by a product wave function in which each "orbital" or one-electron function will depend explicitly on the quantum numbers of all the other electrons. Further he concluded that a purely discrete spectrum is not obtained for the many electron problems.

We shall discuss an eigenvalue transformation that yields an Hermitian operator, which is positive definite. It includes as particular cases, the transformations of Hylleraas and Lundqvist. It is closely related to the variation iteration schemes discussed in Morse and Feshbach[77] and the Sturmian functions of Rotenberg[78] which are

identical with the functions discussed by Hylleraas. The fact that we obtain a positive Hermitian operator implies that we can use the techniques of the preceding chapters, i.e., partitioning, inner projections to our advantage. The results will be applicable to positive or negative perturbations and in general to any perturbation that is decomposable into a positive and a negative part, for bounded H.

6.1. Transformation of the Schrödinger Equation

We can write the Schrödinger equation for an atomic system in the following way:

$$(T+V_e-E_n)\Psi_n = ZV_N\Psi_n \tag{6.1}$$

where T is the electronic kinetic energy operator; V_e, the interelectronic repulsion operator, and $V_N = \sum_{i=1}^{N} r_i^{-1}$. The Ψ_n are square integrable and for a given nuclear charge Z there is a set of eigenvalues E_n with corresponding eigenfunctions Ψ_n. We shall study later the case of molecules.

Consider Eq. (6.1), and instead of Z being given, assume that an energy parameter $\mathcal{E}$ is at our disposal, and that the parameter λ is to be determined for a given $\mathcal{E}$:

$$(T+V_e-\mathcal{E})\Psi = \lambda(\mathcal{E})\, V_N\Psi \quad . \tag{6.2}$$

For $\mathcal{E}$ equal to any of the E_n in Eq. (6.1), i.e., $\mathcal{E} = E_n$, $\Psi_{\mathcal{E}} = \Psi_n$, and Eq. (6.2) must certainly have at least one solution $\lambda(E_n) = Z$. Equation (6.2) is a typical Sturm-Liouville problem, and it should be noticed that Z is the common eigenvalue of a family of operators $L(E_n)$ with corresponding eigenfunctions Ψ_n. In this sense,

the Ψ_n are not degenerate, because they are eigenfunctions to different operators.

Even though Eq. (6.2) is an equation with which we may work, the following transformation provides some insight into its properties. Let

$$\phi_\mathcal{E} = V_N^{\frac{1}{2}}\Psi \quad . \tag{6.3}$$

Then Eq. (6.2) may be written

$$L(\mathcal{E})\phi_\mathcal{E} = V_N^{-\frac{1}{2}}(T+V_e-\mathcal{E})V_N^{-\frac{1}{2}}\phi_\mathcal{E} = \lambda(\mathcal{E})\phi_\mathcal{E} \quad . \tag{6.4}$$

Equations (6.2) and (6.4) have the same eigenvalues $\lambda(\mathcal{E})$. The eigenfunctions are related by Eq. (6.3). Notice that $L(\mathcal{E})$ is an Hermitian operator, therefore if we drop the $\mathcal{E}$ dependence from the notation, Eq. (6.4) may be written:

$$L\phi_n = \lambda_n\phi_n \tag{6.5}$$

and from the properties of Hermitian operators, $L = L^+$, it follows that

$$\begin{aligned} \langle\phi_m|L|\phi_n\rangle &= \lambda_n\langle\phi_n|\phi_n\rangle\delta_{nm} \\ \langle\phi_m|\phi_n\rangle &= \langle\phi_n|\phi_n\rangle\delta_{nm} \end{aligned} \quad . \tag{6.6}$$

From the last equation and Eq. (6.3) it follows that:

$$\langle\phi_m|\phi_n\rangle = \langle\Psi_m|V_N|\Psi_n\rangle = \langle\Psi_n|V_N|\Psi_n\rangle\delta_{nm} \tag{6.7}$$

which expresses the well-known fact that the eigenfunctions of the Sturm-Liouville problem in Eq. (6.2) are orthogonal with respect to the weight factor $V_N = \sum_{i=1}^{N} \frac{1}{r_i} > 0$.

For $\mathcal{E} \leq 0$, as $T \geq 0$ and $V_e \geq 0$ and on account of theorem 1.3 we have

$$L \geq 0 \tag{6.8}$$

which is a fundamental property in what follows. Therefore L is bounded from below, and if it has a partially discrete spectrum, the eigenvalues are positive.

Before discussing the spectrum of L, we will relate the eigenvalues of H and those of L, through an application of the Hellmann[79] and Feynman[80] theorem and indicate how this leads to upper and lower bounds to the E_n.

Consider an eigenvalue problem of the form

$$A = \lambda B\Psi \quad . \tag{6.9}$$

Then

$$\langle\Psi|A-\lambda B|\Psi\rangle = 0 \quad . \tag{6.10}$$

If the operators depend on a parameter $\mathcal{E}$ we may differentiate Eq. (6.10):

$$\langle\frac{\partial\Psi}{\partial\mathcal{E}}|A-\lambda B|\Psi\rangle + \langle\Psi|A-\lambda B|\frac{\partial\Psi}{\partial\mathcal{E}}\rangle + \langle\Psi|\frac{\partial A}{\partial\mathcal{E}}|\Psi\rangle$$

$$- \frac{\partial\lambda}{\partial\mathcal{E}}\langle\Psi|B|\Psi\rangle - \lambda\langle\Psi|\frac{\partial B}{\partial\mathcal{E}}|\Psi\rangle = 0 \quad .$$

If $\frac{\partial B}{\partial\mathcal{E}} = 0$, we obtain

$$\frac{\partial\lambda}{\partial\mathcal{E}} = \langle\Psi|\frac{\partial A}{\partial\mathcal{E}}|\Psi\rangle/\langle\Psi|B|\Psi\rangle \tag{6.11}$$

which is the form of the Hellmann-Feynman theorem that applies in our case. Then.

$$\frac{d\lambda}{d\mathcal{E}} = -\frac{\langle\Psi|\Psi\rangle}{\langle\Psi|V_N|\Psi\rangle} < 0 \quad . \tag{6.12}$$

This is not at all surprising because the function $\mathcal{E} = \mathcal{E}(\lambda)$ has negative slope, i.e., to increase the nuclear charge decreases the energy of an atom. The function $\lambda = \lambda(\mathcal{E})$ is related to the function $\mathcal{E} = \mathcal{E}(\lambda)$, and in fact in certain problems, one can be obtained from the other. In general, it is unwieldy to obtain $\mathcal{E} = \mathcal{E}(\lambda)$; it is the problem of perturbation theory; but in certain cases it is possible to obtain the dependence of the interaction parameter λ on the energy $\mathcal{E}$, and this is the basis for the variation iteration methods of Chapter 9 of Morse and Feschbach. Instead of discussing their approach we will relate upper and lower bounds to $\lambda(\mathcal{E})$ with upper and lower bounds to the E_n. For a given $\mathcal{E}$ there is a series of solutions λ_n. The lowest one is associated with the ground state of the system and so on. If there is any doubt about this, it should be realized that the curves $\lambda(\mathcal{E})$ and $\mathcal{E}(\lambda)$ are the same, and for a given λ, there are many values of $\mathcal{E}$ possible, one for each curve. The lowest one corresponding to the ground state curve. In fact, $\mathcal{E}_o(\lambda)$ is the isoelectronic curve for the ground state as a function of the nuclear charge λ. See figure 7.

Suppose now that we are able, by any method, to provide upper and lower bounds to $\lambda(\mathcal{E})$, i.e., that for any $\mathcal{E}$ we may obtain $\lambda_>(\mathcal{E})$ and $\lambda_<(\mathcal{E})$, such that

$$\lambda_<(\mathcal{E}) \leq \lambda(\mathcal{E}) \leq \lambda_>(\mathcal{E}) \quad . \tag{6.13}$$

We should stress that we are considering a specific state, not necessarily the ground state. The important consequence of Eq. (6.12) is the following:

Theorem 6.1:

If Z is the nuclear charge of the system, and

$$\lambda_<(\mathcal{E}) \leq \lambda(\mathcal{E}) \leq \lambda_>(\mathcal{E})$$

is fulfilled for some state, then any $\mathcal{E}$ that satisfies $\lambda_>(\mathcal{E}) \leq Z$ is an upper bound to the energy E of the state under consideration and any $\mathcal{E}$ that satisfies $\lambda_<(\mathcal{E}) \geq Z$ is a lower bound to it.

The proof follows from the fact that for $\lambda_>(\mathcal{E}) \leq Z \equiv \lambda(E)$, $E \leq \mathcal{E}$ because of the negative slope of λ. Similarly for the lower bound: if $\lambda_<(\mathcal{E}) \geq Z \equiv \lambda(E)$ it follows that $\mathcal{E} \leq E$. See figure 8.

Therefore upper bounds to $\lambda(\mathcal{E})$ are related to upper bounds to E and the same applies to the lower bounds. We should realize now that this treatment is applicable to any negative part of the Hamiltonian. One has to repeat the derivation that starts in Eq. (6.2), where instead of λ being the nuclear charge and $V = \sum \frac{1}{r_i}$, λ is an artificial strength parameter and -V is a negative part of the Hamiltonian. The pertinent modification of theorem 6.1 is that Z is replaced by 1, or by the appropriate constant according to the circumstances.

So far there is nothing done towards solving Eq. (6.1), because Eqs. (6.2) or (6.5) are just as difficult. But as L is positive, actually, as any part of L is positive by construction, it is possible to carry inner projections of L, or of parts of L, which are a necessary tool in obtaining lower bounds to $\lambda(\mathcal{E})$. In addition it is possible to split L into an unperturbed part, with known spectrum and a positive perturbation. In the case of one-electron systems, the spectrum is discrete. For many electron systems, the spectrum is partially discrete

and partially continuous. In the next section, we study the spectrum with some detail.

6.2. Nature of the Spectrum

The spectrum associated with Eq. (6.2) and Eq. (6.4) can be studied by considering first the unperturbed problem associated to them, namely, the one obtained by neglecting the interelectronic repulsion. Therefore we set:

$$L^{o} = V_N^{-\frac{1}{2}}(T-\mathcal{E})V_N^{-\frac{1}{2}} , \quad \mathcal{E} < 0 \quad . \tag{6.14}$$

Both T and V are sum of one electron operators:

$$T = \sum_i T(i); \quad V_N = \sum_i V(i) \quad . \tag{6.15}$$

Equation (6.2) is then

$$\sum_i [T(i)-\lambda^{o}V(i)]\Psi^{o} = \mathcal{E}\Psi^{o}, \quad \mathcal{E} < 0 \quad . \tag{6.16}$$

The problem is to find solutions λ^{o} and Ψ^{o} for a given $\mathcal{E}$. As antisymmetry was a condition on the solutions of Eq. (6.1) we shall impose the same requirement on Ψ^{o}. We purposely will ignore all other questions of symmetry of the solutions of Eq. (6.16). As the operator involved is a sum of one electron operators, we may seek solutions in the form of antisymmetized products of spin orbitals, i.e., construct determinants, take linear combinations of them in order to construct eigenfunctions of L^2, S^2, etc. But for our purposes it is enough to assume that all that can be done following the treatment given in the book by Slater [81].

Let A be the antisymmetrizer operator. We seek solutions of the form

$$\Psi^{o} = A\prod_{j} u_{j}(j) \quad . \tag{6.17}$$

Replacing Eq. (6.17) in Eq. (6.16) we obtain

$$A\sum_{i}\prod_{j\neq i} u_{j}(j)[T(i)-\lambda^{o}V(i)]u_{i}(i) = \mathcal{E}\Psi^{o} \quad , \tag{6.18}$$

where we have used the fact that the antisymmetrizer commutes with the symmetric operators T and V_N. Let us set $\mathcal{E} = \sum_{i} \mathcal{E}_{i}$, where the $\mathcal{E}_{i}$'s are entirely arbitrary. Then Eq. (6.18) becomes

$$A\sum_{i}\prod_{j\neq i} u_{j}(j)[T(i)-\lambda^{o}V(i)-\mathcal{E}_{i}]u_{i}(i) = 0 \ . \tag{6.19}$$

This allows us to assert that Eq. (6.17) is a solution of Eq. (6.16) provided that the following conditions are fulfilled:

$$\begin{aligned} &\text{(i)} \quad \mathcal{E} = \sum_{i} \mathcal{E}_{i} < 0 \\ &\text{(ii)} \quad [T(1)-\lambda_{i}^{o}V(1)-\mathcal{E}_{i}]u_{i}(1) = 0 \\ &\text{(iii)} \quad \lambda_{i}^{o} = \lambda^{o} \quad \text{for all } i \end{aligned} \tag{6.20}$$

Consider condition (ii). If $V(1) = r_1^{-1}$, it is entirely analogous to the hydrogen atom eigenvalue problem, but with the energy as a fixed arbitrary parameter and the nuclear charge as the eigenvalue to be determined.

If one uses the method of Frobenius to solve (ii) one finds the same terminating condition for the series as in the hydrogen

atom case, namely that

$$\lambda_i^o = n\sqrt{-2\varepsilon_i}, \quad n=1,2,\ldots, \infty \ . \tag{6.21}$$

The eigenfunctions are hydrogen-like functions, but with no dependence on the quantum number n in the argument:

$$u_i = u_{n_i \ell_i m_i} = R_{n_i \ell_i}(\sqrt{-2\varepsilon_i}\, r_1)\ Y_{\ell_i m_i}(\theta_i, \psi_i) \tag{6.22}$$

These functions were already known by Schrödinger.[74] The fact that they form a complete, discrete, set was used by him and by others.[75] There is a discussion by Hylleraas[82] of a transformation of the Schrödinger equation for the S-states of the hydrogen atom which yields essentially the same solutions as Eqs. (6.21) and (6.22), and where he proves the completeness of the discrete spectrum of (ii) for $\varepsilon_i < 0$. Clearly, they are orthogonal with weight factor $V(1) = r_1^{-1}$. For a more detailed discussion of different basis sets, and contribution of the continuum, see page 274 of reference [36]. In the present context the significant point is that for a one-electron problem and one center the transformation being discussed yields a complete discrete spectrum. Unfortunately this does not follow for many electron problems. Consider condition (i) of Eq. (6.20). The sum of "one-electron energies" can be negative even if one, or at the most, n-1 of them are positive. Therefore, there are solutions of Eq. (6.16) which correspond to positive ε_i and these form a continuum. At any rate let us consider the discrete part of the spectrum and examine the solutions in more detail. We have to impose condition (iii) Let the ε_i's satisfy

$$\mathcal{E}_i = \epsilon p_i^2, \quad \epsilon < 0. \tag{6.23}$$

Then Eq. (6.21) becomes

$$\lambda_i^o = n_i p_i \sqrt{-2\epsilon} \tag{6.24}$$

The p_i's are integers at our disposal. Let's denote a set of p_i's by $p = \{p_i\}$. Then, given a set p, we impose a restriction on the associated n_i's:

$$n_i p_i = nM(p), \qquad n=1,2,\ldots,\infty , \tag{6.25}$$

where M(p) is the lowest common multiple of the set p. In such a case Eq. (6.24) becomes

$$\lambda_i^o = \lambda_{n,p}^o = nM(p)\sqrt{-2\epsilon}, \quad \text{for all } i. \tag{6.26}$$

We see then that the set p determines a "configuration," and for each configuration there is a set of eigenvalues $\lambda_{n,p}^o$, and a set of eigenfunctions, antisymmetized products of spin orbitals, where the radial functions are given by Eq. (6.22) provided the condition in Eq. (6.25) is imposed on the indices n_i. The eigenfunctions are given by

$$\Psi^o = \Psi_{n,p}^o = A \prod_i R_{n_i \ell_i m_i}(p_i\sqrt{-2\epsilon}\, r_i) Y_{\ell_i m_i}(\theta_i, \psi_i) \begin{Bmatrix} \alpha(i) \\ \beta(i) \end{Bmatrix} \tag{6.27}$$

where

$$n_i = \frac{M(p)}{p_i} .$$

We should notice that this shows explicitly how each one-electron function which appears in the solutions of Eq. (6.2) depends on the quantum numbers of all the other spin orbitals as suggested by Lundqvist. It should be emphasized that not all choices of the set p

are independent. For a given $\mathcal{E}$, there is a restriction on any set p':

$$\mathcal{E} = \epsilon \sum_i p_i^2 = \epsilon' \sum_i p_i'^2 \tag{6.28}$$

or

$$\epsilon' = \epsilon \sum_i p_i^2 / \sum_i p_i'^2 \ . \tag{6.29}$$

Therefore, for any set p', the eigenvalues $\lambda^o_{n,p'}$ are related to the eigenvalues $\lambda^o_{n,p}$ by:

$$\lambda^o_{n,p'} = nM(p')\sqrt{-2\epsilon'} = nM(p)\sqrt{-2\epsilon}\ \frac{M(p')}{M(p)} \sqrt{\frac{\sum p_i^2}{\sum p_i'^2}} \ . \tag{6.30}$$

Any choice p' such that $p_i' = \alpha p_i$ should be discarded because, by Eq. (6.30) does not give anything new. If $p_i = \alpha p_i$; $M(p') = \alpha M(p)$ and $\lambda^o_{n,p'} = \lambda^o_{n,p}$.

For the two-electron problem the choices of "configurations" p are : (1,1), (1,2), (1,3), ...; (2,3), (2,5), (2,7), ...; (3,4), (3,5), (3,7), ..., etc. Each configuration will lead to a set of solutions by letting n assume the values $1,2,3,\ldots,\infty$.

The discussion of the full operator L should have the preceding as a starting point, but for our purposes it is sufficient to have found an unperturbed operator with a partially discrete spectrum, with known solutions and therefore tractable by the methods of the preceding chapter. We have not obtained a similar solution for the molecular

case, but we shall take advantage of the completeness of the one-electron solutions in conjunction with the method of truncations in a later section.

6.3. Atomic Systems

The fact that starting from the Schrödinger equation we have obtained a positive definite Hermitian operator has several useful consequences that we will discuss in this section.

First we shall construct an inner projection of the operator L:

$$\begin{aligned} L &\equiv V_N^{-\frac{1}{2}})T+V_e-\mathcal{E})V_N^{-\frac{1}{2}} \\ &\equiv V_N^{-\frac{1}{2}}MV_N^{-\frac{1}{2}} \quad . \end{aligned} \tag{6.31}$$

For $\mathcal{E} < 0$, $M > 0$. Therefore, by theorem 1.9, we can construct an inner projection M' which fulfills the following:

$$M' = M^{\frac{1}{2}}QM^{\frac{1}{2}} \leq M \quad , \tag{6.32}$$

where Q is an arbitrary projection operator.

We can define now

$$L' \equiv V_N^{-\frac{1}{2}}M'V_N^{-\frac{1}{2}} \quad , \tag{6.33}$$

which, by theorem 1.3, implies

$$L' \leq L \quad . \tag{6.34}$$

From theorem 1.2, it follows that the eigenvalues of L' are, in order, smaller than those of L, i.e.

$$L'\phi_i' = \lambda_i'\phi_i'; \quad L\phi_i = \lambda_i\phi_i; \quad \lambda_i' \leq \lambda_i \quad . \text{ in order} \tag{6.35}$$

The importance of this is that we can, if we wish, incorporate the Schrödinger equation to the host of problems that can be treated directly by the method of intermediate problems, without appealing to truncations or splitting the Hamiltonian into a perturbed and an unperturbed part. Thus we can set, $Q = |\mathfrak{f}\rangle\Delta^{-1}\langle\mathfrak{f}|$, where $\mathfrak{f}$ is an arbitrary linear manifold, and Δ it's overlap, or metric matrix. Let's transform to the following manifold: $M^{\frac{1}{2}}|\mathfrak{f}\rangle = M|g\rangle$, the Aronszajn space. Then we may write:

$$L' = V_N^{-\frac{1}{2}}M|g\rangle\Delta^{-1}\langle g|MV_N^{-\frac{1}{2}} \tag{6.36}$$

where the metric matrix is given by:

$$\Delta = \langle g|M|g\rangle \quad . \tag{6.37}$$

With this projection, the eigenvalue problem of L' becomes:

$$V_N^{-\frac{1}{2}}M|g\rangle\Delta^{-1}\langle g|MV_N^{-\frac{1}{2}}|\phi'\rangle = \lambda'|\phi'\rangle \tag{6.38}$$

or

$$MV_N^{-1}M|g\rangle\Delta^{-1}\langle g|MV_N^{-\frac{1}{2}}|\phi'\rangle = \lambda' MV_N^{-\frac{1}{2}}|\phi'\rangle$$

which implies:

$$[\langle g|MV_N^{-1}M|g\rangle\Delta^{-1} - \lambda'\mathbb{1}]\cdot\langle g|MV_N^{-\frac{1}{2}}|\phi\rangle = 0 \ . \tag{6.39}$$

Therefore, we have non-trivial solutions for

$$\det\{\langle g|MV_N^{-1}M|g\rangle\Delta^{-1} - \lambda'\mathbb{1}\} = 0$$

or explicitly:

$$\{\langle g|(T+V_e-\mathcal{E})V_N^{-1}(T+V_e-\mathcal{E})|g\rangle - \lambda'\langle g|T+V_e-\mathcal{E}|g\rangle\} = 0. \tag{6.40}$$

The roots of the secular determinant Eq. (6.40) are, in order, lower bounds to the eigenvalues of Eq. (6.31), provided $\mathcal{E} < 0$.

Furthermore, by our theorem 6.1, any lower bound $\lambda' \geq Z$ obtained for a specific value of $\mathcal{E}$, implies that $\mathcal{E}$ is a lower bound to the energy of that state. In particular, the lowest root of Eq. (6.40) is associated with a lower bound $\mathcal{E}$, to the energy of the ground state of the system provided that $\lambda'(\mathcal{E}) \geq \lambda(E_o) = Z$.

Another alternative is to divide L into two parts L_o and L_V, where

$$L = L_o + L_V; \quad L_o = V_N^{-\frac{1}{2}}(T- \;)V_N^{-\frac{1}{2}}; \quad \mathcal{E} < 0,$$
$$L_V = V_N^{-\frac{1}{2}} V_e V_N^{-\frac{1}{2}} = V_N^{-1} V_e = V_e V_N^{-1} \quad . \tag{6.41}$$

The operators L_o and L_V are both positive. L_o has a known spectrum, which, as we saw in the previous section, is partially discrete. It would be interesting to compare the nature of truncations of L_o with those of H_o. In fact, we may apply any of the methods discussed previously, perturbation methods combined with inner projections, partitioning, etc. For the sake of comparison with the intermediate problems we will derive the secular equation corresponding to a truncation of L_o. We might just as well obtain the partitioning solution, but we want to show in one case the characteristic method of arriving at the secular equation. We will use a Bazley projection of L_V:

$$L_V > L_V' \equiv |\mathbb{h}\rangle \Delta^{-1} \langle \mathbb{h}|, \quad \Delta = \langle \mathbb{h}| V_N V_e^{-1} |\mathbb{h}\rangle \quad .$$

The linear manifold $\mathbb{h}$ is at our disposal, and for simplicity, though by no means necessary, we will choose it as comprising p eigenfunctions to L : $\mathbb{h} = \mathbb{\phi}^o = \{\phi_1^o, \phi_2^o, \ldots, \phi_p^o\}$.

A natural truncation of L_o is, in this case,

$$L_o > L'_o = \sum_{n=1}^{p} |\phi_n^o\rangle \lambda_n^o \langle \phi_n^o| \quad .$$

Compare with Eqs. (6.3), (6.26) and (6.27). Notice that the truncation yields an operator L_o, smaller than L_o without including the orthogonal complement to the subspace $\mathcal{P}^o$. This is because $L_o > o$, and it avoids integrals of the type in Eq. (5.32).

We may arrange the eigenvalues of L_o included in the truncation in a square matrix:

$$(\lambda^o)_{ij} = \lambda_i^o \delta_{ij} \quad . \tag{6.42}$$

Then we have

$$L > L' \equiv |\mathcal{P}^o\rangle \lambda^o \langle \mathcal{P}^o| + |\mathcal{P}\rangle \Delta^{-1} \langle \mathcal{P}| \quad . \tag{6.43}$$

The eigenvalue problem for L' is:

$$|\mathcal{P}^o\rangle (\lambda^o + \Delta^{-1}) \langle \mathcal{P}^o | \phi' \rangle = \lambda' \phi' \tag{6.44}$$

which means

$$\langle \mathcal{P}^o | \mathcal{P}^o \rangle (\lambda^o + \Delta^{-1}) - \lambda' \, \mathbb{1} | = 0$$

or

$$| \lambda^o + \Delta^{-1} - \lambda' \, \langle \mathcal{P}^o | \mathcal{P}^o \rangle^{-1} | = 0 \quad . \tag{6.45}$$

In terms of the set $\psi_n^o = V_N^{-\frac{1}{2}} \phi_n^o$,

$$| \lambda^o + \langle \Psi^o | V_e^{-1} | \Psi^o \rangle^{-1} - \lambda^{-1} \langle \Psi^o | V_N | \Psi^o \rangle | = 0 \, . \tag{6.46}$$

We have to remember that the condition on the eigenvalues λ_i' is $\lambda_i' \leq \lambda_i$, in order, so if we use theorem 6.1, any value of $\mathcal{E}$ such that $\lambda_1'(\mathcal{E}) \geq \lambda_1(E) = Z$ is a lower bound to the ground state.

It is clear that we can develop a partitioning approach for obtaining upper and lower bounds to the eigenvalues of L, starting from the zero order operator L^o. We do know its lowest eigenvalues and eigenfunctions, and the perturbation is positive. This is of some interest and warrants some future work, yet its use does not seem to simplify any of the problems that, in the atomic case, can be solved in the conventional way. On the other hand, in the case of negative perturbations it may prove to be very useful.

6.4. Molecular Problems

To finish this brief review of applications of the transformation indicated in section 6.1, we consider now molecular problems.

First of all, we should point out that the main difficulty in treating molecular problems is the absence of a splitting of the Hamiltonian into an unperturbed part with partially known spectrum and a positive perturbation. From what was said in the previous sections, we should be able to treat splittings involving negative perturbations.

Bazley and Fox[72] suggested a treatment for molecules that seem to bypass the problem, but it pays the price of introducing truncations and this, as we say in Chapter V, restricts the accuracy of the approach when the operator being truncated does not have a complete

discrete spectrum. It should be clear by now what we look for: an eigenvalue transformation that should allow the use of truncations, with hope of convergence to the exact eigenvalues. We'll see how this is achieved and how truncations may be avoided completely.

We shall first sketch the treatment due to Bazley and Fox. There are several qualifications on the applicability of the method in terms of spectrum, domains, limit points, etc., of the Hamiltonians involved, but we shall refer to their paper for details. We shall assume that the spectra of H^o and H, as we will define later, have a set of low lying, discrete eigenvalues below the first accumulation point of H. For simplicity we shall consider a molecular system for a given configuration of the nuclei and we thus are treating the electronic molecular problem within the Born-Oppenheimer approximations, and this, if solved exactly would lead to a lower bound to the molecular energy[83,84]. Since the Laplacian is invariant under translations of the coordinate origin we may write for the electronic Hamiltonian:

$$H = \sum_{\alpha=1}^{n} \sum_{i=1}^{m} \left(-\frac{a_{i\alpha}\Delta_{i\alpha}}{2} - \frac{Z_\alpha}{r_{i\alpha}}\right) + \sum_{i<j}^{m} \frac{1}{r_{ij}} \tag{6.47}$$

$$= H_o + V = \sum_{\alpha=1}^{n} \sum_{i=1}^{m} H_{i\alpha} + \sum_{i<j}^{m} \frac{1}{r_{ij}}$$

where

$$\sum_{\alpha}^{n} a_{i\alpha} = 1, \qquad i=1,2,\ldots,m \quad . \tag{6.48}$$

The α's label the n nuclei, and the i's label the m electrons. The operator $\Delta_{i\alpha}$ is the Laplacian of electron i expressed with the nucleus α as original. The $a_{i\alpha}$ are arbitrary positive real numbers that satisfy Eq. (6.48).

We certainly have a splitting into an unperturbed Hamiltonian and a positive perturbation, but the unperturbed part has no known spectrum or analytic solutions. In fact for two centers and one electron, our zero order Hamiltonian is just the H_2^+ Hamiltonian. We may write it:

$$H = (-\tfrac{1}{4}\nabla^2_{1a} - \frac{1}{r_{1a}}) + (-\tfrac{1}{4}\nabla^2_{1b} - \frac{2}{r_{1b}})$$

$$= \tfrac{1}{2}\left\{(-\tfrac{1}{2}\nabla^2_{1a} - \frac{2}{r_{1a}}) + \tfrac{1}{2}(-\tfrac{1}{2}\nabla^2_{1b} - \frac{2}{r_{1b}})\right\} = H_a + H_b \qquad (6.49)$$

where we have set $a_{1a} = a_{1b} = \frac{1}{2}$.

What Bazley and Fox have done is suggested by Eq. (6.49). Even though we do not have analytic solutions for Eq. (6.49), we can introduce truncations in the operators H_a and H_b, both with known, hydrogen-like spectrum.

The natural truncation will be in this case:

$$H_a^{(p)} = \sum_{\ell=0}^{p} E_\ell^{(a)} O_\ell^{(a)} + E_{p+1}^{(a)}\Big(1 - \sum_{\ell=0}^{p} O_\ell^{(a)}\Big) \leq H_a \qquad (6.50)$$

where $E_\ell^{(a)} = -\frac{1}{\ell^2}$ in the case of Eq. (6.49). Similarly for Eq. (6.47) we may write:

$$H = H_o + V \geq \sum_{\alpha=1}^{n}\sum_{i=1}^{m} H^{(p)} + \sum_{i<j}^{m} \frac{1}{r_{ij}} \qquad (6.51)$$

where

$$H_{i\alpha}^{(p)} = a_{i\alpha}\left\{\sum_{\ell=0}^{p} E_{i,\ell}^{(\alpha)} O_{i,\ell}^{(\alpha)} + E_{i,p+1}^{(\alpha)}\left(1-\sum_{\ell=0}^{p} O_{i,\ell}^{(\alpha)}\right)\right\} \tag{6.52}$$

where

$$E_{i,\ell}^{(\alpha)} = -\frac{Z_\alpha^2}{2a_{i\alpha}\ell^2} \tag{6.53}$$

and the projectors $O_{i,\ell}^{(\alpha)}$ are given by

$$O_{\ell}^{(\alpha)} = |\Psi_{i\ell}^{(\alpha)}\rangle\langle\Psi_{i\ell}^{(\alpha)}| \tag{6.54}$$

where $\Psi_{i\ell}^{(\alpha)}$ are just hydrogen-like functions centered at the nucleus α.

It is clear that this method of truncations, in conjunction with the formulae of Chapter V will lead to lower bounds to the electronic energy. Further, if one applies inner projections to V, and chooses suitable linear manifolds, lower bound formulae with simple integrals to compute are obtained[85].

Instead of proceeding further along this line, and we refer to Bazley and Fox,[72] we want to point out that this procedure cannot converge to the exact results because the truncations leave out the whole continuum portion of $H_{i\alpha}$, and increasing p will lead to a limited improvement.

Johnson and Coulson[73] have applied the truncations defined by Eq. (6.52) to the H_2^+ molecule Hamiltonian, Eq. (6.49), and obtained very poor convergence. We list their results for g and u states as a

function of p in Eq. (6.52)

order of truncation p:	1	3	6	Exact Energy
g states(1)	-1.390	-1.320	-1.300	-1.103
(2)		-0.451	-0.438	-0.361
(3)		-0.300	-0.271	-0.236
(4)			-0.214	-0.178
u states(1)	-1.110	-1.004	-0.969	-0.668
(2)		-0.370	-0.346	-0.255
(3)		-0.224	-0.193	-0.137
(4)			-0.136	-0.127

The exact energies are taken from Bates, et al.[86].

The method is appealingly simple, i.e., one has to evaluate a set of overlap integrals only, because the operator involved is just $H_a^{(p)} + H_b^{(p)}$. But the price of neglecting the continuum in the truncations seems to be too high.

What we should notice is that we may write the Schrödinger equation for the H_2^+ molecule in the form

$$\left\{\left(-\frac{1}{2}\nabla_{1a}^2 - \frac{2}{r_{1a}} - E\right) + \left(-\frac{1}{2}\nabla_{1b}^2 - \frac{2}{r_{1b}} - E\right)\right\}\Psi = 0. \qquad (6.55)$$

Now instead of considering E as the eigenvalue, we replace it by an energy variable $\mathcal{E}$, at our disposal and replace the "nuclear charge" 2 by a parameter λ to be determined. We have then

$$\left\{\left(-\frac{1}{2}\nabla_{1a}^2 - \frac{\lambda}{r_{1a}} - \mathcal{E}\right) + \left(-\frac{1}{2}\nabla_{1b}^2 - \frac{\lambda}{r_{1b}} - \mathcal{E}\right)\right\}\Psi = 0. \qquad (6.56)$$

But each term in parenthesis is exactly of the same nature as the operator in the second equation of Eq. (6.20). It has a complete,

discrete spectrum. We may apply truncations and expect to converge faster than before to the exact eigenvalue, determined by theorem 6.1.

Calculations of this sort were reported by Walmsley[11] and the results were the following:

p = 1	p = 3	p = 6	exact
-1.267	-1.140	-1.119	-1.103

Only the ground state was treated and the results should be compared with the ones obtained by Coulson and Johnson. We see then, that this particular case of the eigenvalue transformation in Eq. (6.2) applied to molecules shows fast convergence, and this is very promising, especially since the truncation method, following the Bazley and Fox idea is not the only way to proceed. In fact, the only requirement is that theorem 6.1 should be implemented in some way or another. So we may write the eigenvalue problem for the molecule in the form:

$$\left\{ \sum_{\alpha=1}^{m} \sum_{i=1}^{n} \left(-\frac{a_{i\alpha}}{2} \nabla_{i\alpha} \right) + \sum_{i<j}^{n} \frac{1}{r_{ij}} - E \right\} \Psi = \sum_{\alpha=1}^{m} \sum_{i=1}^{n} \frac{Z_\alpha}{r_{i\alpha}} \Psi \ . \qquad (6.57)$$

We carry out an eigenvalue transformation of this equation, and replace E by an arbitrary energy $\mathcal{E}$, and we solve for an eigenvalue parameter that multiplies the right hand side of Eq. (6.57). Theorem 6.1 is implemented by imposing

$$\lambda_<(\mathcal{E}) \geq \lambda(E) \equiv 1.$$

and we can treat the modified version of Eq. (6.57) in several ways. Further, we may separate any part of the nuclear attraction as the "negative" part of the Hamiltonian. An interesting form is given by the following, where for simplicity we consider the H_2 molecule:

$$\left\{\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a_1}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{a_2}}\right) + \frac{1}{r_{12}} - \mathcal{E}\right\}\Psi = \lambda\left(\frac{1}{r_{b_1}} + \frac{1}{r_{a_2}}\right)\Psi$$

or

$$\left\{\left(H_a - \frac{\mathcal{E}}{2}\right) + \left(H_b - \frac{\mathcal{E}}{2}\right) + \frac{1}{r_{12}}\right\}\Psi = \lambda\left(\frac{1}{r_{b_1}} + \frac{1}{r_{a_2}}\right)\Psi \quad . \tag{6.58}$$

Each of these splittings has to be explored further. At the moment we may say that they may be treated by a wide assortment of possible methods, some similar to the one derived in the previous section, which was obtained by an inner projection of the positive part of the Hamiltonian. One may apply perturbation methods, either combined with truncations, with results similar to those of Chapter V and of Eq. (6.56). For H_2^+, this is simple and successful. If the difficult integrals that appear when one uses truncations are to be avoided one should carry an inner projection of the interelectronic repulsion and obtain, for conveniently selected manifolds, simple secular equations.[86]

What is the role of partitioning in this case? Twofold: it provides explicit solutions to the secular problems that arise from truncations and more important, it can bypass the intermediate problems by choosing convenient manifolds in the inner projections. We only need an unperturbed Hamiltonian, with a partially discrete spectrum, and a perturbation which must be just a sum of a positive and a negative part.

The positive part may be treated by the conventional inner projection technique, and the negative part by applying the method suggested in this chapter. This is, in fact, a starting point for future work.

CHAPTER VII

DISCUSSION

In the preceding chapters we have made a sketchy survey of the present status of the partitioning technique and lower bound theory. Actually we have almost neglected some of the most important aspects, like multidimensional partitioning and we have focused the attention on some specific problems. This is rather preliminary in the sense that further work, both formal and numerical, should be done, yet it seems worthy to review the results obtained so far because they hint at new problems and applications.

Perhaps, we should stress that lower bound calculations have not only a formal value, but they may settle questions with direct physical significance. For instance, some doubly excited states of Li have been spectroscopically identified with the help of simple lower bound criteria [87]; lower bound to the repulsion energy of two He atoms in the short distance range would be very helpful, if accurate enough, to discuss the effects of non-adiabaticity.

Properties other than energy, calculated as expectation values over variational functions or by low order perturbation theory span a field where the theory of upper and lower bounds should be applied in order to have a reasonable confidence in the significance of the comparison of calculated and experimental properties. It is well-known that improved variational functions do not, by any means, insure better

expectation values [88,89]. It is hoped that further study of operator inequalities, of the type indicated in Chapter I will be useful. In fact some of the conditions being used are too strong, i.e., instead of positive operators we need only to consider operators in their domains of positivity, etc.

In Chapter II, we showed that the well-known formula for lower bounds to the ground state due to Temple arises from a truncation of the spectral resolution of the reduced resolvent operator T, fundamental tool of the partitioning approach. This indicates under what conditions the partitioning approach may yield a better bound and a way of removing one of the drawbacks of Temple's formula, namely, the requisite of knowing the first excited eigenvalue of H. The partitioning approach shows that one actually needs a lower bound to the ground state of PHP, where P is the projection operator of the orthogonal complement to ψ, the reference function under consideration. Lower bounds to the eigenvalues of PHP were shown to be useful in estimating the Weinstein function Eq. (1.26), as in Eq. (1.29) and Eq. (2.10). The Weinstein function is the key quantity in the full resolvent technique and recent work by Sasakawa [90] using Green's functions and dispersion relations may be implemented through the explicit calculation of the Weinstein function. In Chapter V we have obtained, by using the partitioning technique to solve the intermediate problems arising from truncations, formulae that give the desired lower bounds to the eigenvalues of PHP. A problem related to obtaining bounds to the eigenvalues of H and PHP is the accuracy of approximate wave functions for the ground and excited states. We have reviewed briefly

several formulae existing in the literature and trivally verified that the bounds are not necessarily very good in a simple test case. The formulae require lower bounds to the excited states, and hence this warrants calculations of lower bound for excited levels.

In Chapter III we show an explicit solution of the inhomogeneous equations that arise from a truncation of the reduced resolvent T_o associated with the unperturbed Hamiltonian H_o. It provides a solution to all orders, avoiding the pitfalls of Brillouin-Wigner low order perturbation theory. The truncation is related to the variational principle and by applying successive partitioning technique we obtain the Feenberg perturbation series directly. This derivation stresses the fact that the Feenberg expansion is a bracketing function in the sense of Eq. (1.12), i.e., it is an implicit relation $\mathcal{E}_1 = f(\mathcal{E})$, and $\mathcal{E}_1$ and $\mathcal{E}$ bracket the eigenvalue E. As it is well known,[56] successive partitioning technique assumes a particular simple form for triple diagonal matrices.

There are certain problems where the Hamiltonian matrix has that form: Mathieu problem, anharmonic oscillator, linear chains with nearest neighbour interactions, and any finite symmetric matrix can be brough to triple diagonal form in a finite number of steps. We have shown that the recurrence relation derived by Nordling[56] can be expressed as a continued fraction, and this is an alternate derivation of the continued fraction representation of the solutions of the Mathieu problem. We believe that this may be exploited computationally in the solution of eigenvalue problems and in the treatment of systems with nearest neighbour interactions.

In Chapter IV we have reviewed the theory of reciprocal variational problems and how it may be applied to quantum mechanical problems through inhomogeneous equations like those appearing in perturbation theory. This allowed a new derivation of the lower bound formulae for the even order energies in Rayleigh-Schrödinger theory, originally due to Hirschfelder and Prager by analogy with electromagnetic theory. The upper bound formulae for the even order energies, in both Rayleigh-Schrödinger and Brillouin-Wigner theory, due originally to Hylleraas, find a natural place in the present formalism, and the extension to excited states follows naturally from this essentially geometrical approach.

Chapter V contains a discussion of another truncation of T_o, which leads to a set of partitioning formulae that yield explicit solutions to the secular equations of the intermediate problems. In that sense they are formally equivalent, yet we should point out that the partitioning solutions allow us to bypass the secular problem. Furthermore they provide, also, a set of lower bounds to the eigenvalues of PHP. This comes about by searching the asymptotes to the bracketing function. This important byproduct, useful within the context of Chapter II, is not obtained in the conventional method of solving the secular equation of the intermediate problems.

We should emphasize here that the truncations of Chapter III and V are not the only tools available to compute the bracketing functions of the partitioning technique. The multiple dimensional partitioning technique combined with inner projections of positive operators has proven to be extremely successful, as shown by Choi [71]. He applied

transformations of the inner projection space suggested by Löwdin in PTXI, and obtained very good results for He like ions including H^-, which is a pathological case in the intermediate Hamiltonian approach due to the ordering theorem 1.2.

The eigenvalue transformation introduced in Chapter VI includes, as particular cases, transformations known to Schrödinger[74] and Hylleraas[82]. For one-electron problems, it yields a complete discrete spectrum when applied to a central field. We showed that in the many-electron case the one-electron functions depend on the quantum numbers of the set of spin orbitals defining the state, as stated by Lundqvist[76] and that the transformation does not give a complete discrete spectrum in this case, but it yields a continuum, too.

As an Hermitian positive operator is generated, we may apply the standard techniques. This leads to several formulae for lower bounds. We have shown how the method is applicable, in principle, to molecules. They may be treated in several ways, one of which is by truncations of the type introduced by Bazley and Fox[88] for the calculation of lower bounds to molecules. The main difference, and it is not a trivial one, is that the truncations are made on operators with a complete, discrete spectrum. It was drawn to our attention that calculations on H_2^+, made by Walmsley[11], fall into this scheme. If we compare them with an analogous truncation method for H_2^+, carried by Johnson and Coulson[73], we see the superiority of the former approach, and it can be ascribed to the neglect of the continuum in the latter.

We have discussed a host of problems that arise in the application of partitioning technique to the calculation of upper and lower bounds to atomic and molecular systems. It is felt that much work has to be performed in the future, in the areas of properties other than energy and in the molecular systems. Further development of the formal inequalities and spectral resolutions is needed. The inhomogeneous equation approach is very forceful, and some systems may be treated by the continued fraction approach inherent to triple diagonal matrices. The case of negative perturbations and the approach to molecular systems that follow from the last chapter are certainly of much interest and will be further studied.

After completing this dissertation, the work by Swalen and Pierce[91] was brought to our attention. Their treatment of triple diagonal matrices leads to a continued fraction calculation of the eigenvalues, and in fact, the results are identidical to ours. On the other hand, the successive pivotal condensations they employ or the elimination method, can be cast within the framework of successive partitioning technique, and this is the basis for the study of the convergence properties, and it would be valuable to repeat and extend their discussion taking advantage of this fact.

APPENDIX I

In this appendix, we illustrate some of the properties of the bracketing function $\mathcal{E}_1 = f(\mathcal{E})$, in particular the convergence as determined by the derivative $f'(\mathcal{E})$. For the present purpose, it is convenient to choose a case where the exact solutions are known. Thus we choose a simple secular equation for the He atom, and use antisymmetized products of hydrogen-like functions as a basis. We proved in Chapter II that the partitioning solution is given by the truncation $T_o'(p)$ as defined in Eq. (3.36) and Eq. (3.37). The corresponding system of linear equations in Eq. (3.39) can be solved by iteration.

These calculations are described in reference [92]. It is convenient but by no means necessary to express the bracketing function corresponding to Eq. (3.37) in terms of the energy shift only, i.e., for a state g:

$$\mathcal{E}'_{1,q} = E_q^o + \langle \psi_q^o | V^{-1} T_o'(p) | \psi_q^o \rangle = E_q^o + t'_{qq}(p). \tag{A.1}$$

where

$$T_o'(p) = \sum_{\substack{k=o \\ k \neq q}}^{p} \frac{O_k^o}{\mathcal{E} - E_k^o} \tag{A.2}$$

Then by applying successive partitioning, we may obtain an implicit equation for $t_{qq}(3)$. This is done by triangularizing the system of equations in Eq. (3.44), which in fact, yields the Feenberg approximant for a limited basis of eigenfunctions to H_o, as we have

shown in Chapter III. Given $t'_{qq}(p) = f(t'_{qq}(p))$, the derivative f' follows easily and for the case of p = 3, it has the form which we gave in reference [92].

$$f'(\mathcal{E}) = [V_{q\ell}^2 V_{\ell m}^2 + V_{qm}^2 V_{\ell m}^2 + V_{q\ell}^2 \gamma_{qm}^2 + V_{qm}^2 \gamma_{q\ell}^2 + 2V_{qm} V_{m\ell} V_{\ell q}(\gamma_{q\ell}+\gamma_{qm})][\gamma_{q\ell} + \gamma_{qm} - V_{m\ell}^2]^{-2} \tag{A.3}$$

where

$$\gamma_{qj} = \mathcal{E}_q - E_j^o - V_{jj}, \quad j \neq q$$

and the subindices q, ℓ, and m may have the values 1, 2, or 3 with the restrictions that $q \neq \ell, m$, $m \neq \ell$.

Using as a basis the configurations $(1s)^2$, (1s)(2s) and $(2s)^2$, with scale factor z = 2, which amounts to having as a perturbation $V = \frac{1}{r_{12}}$, we plotted (A.3) as a function of $\mathcal{E}$ for q = 1, 2, and 3. From (A.3) it is easy to derive the condition for f' to blow up. It is, with the same injunctions on the indices as in (A.3)

$$\gamma_{q\ell} + \gamma_{qm} - V_{m\ell}^2 = 0 \quad . \tag{A.4}$$

We will see that the values of $\mathcal{E}$ for which the bracketing function $\mathcal{E}_{1,q}$ blows up are very close to the values $E'_k = f(E'_k)$, $k \neq q$, i.e., to the other roots of the secular equation.

The convergence condition for the iterative method of solution is given by Eq. (1.15), i.e., the procedure converges if $f'(\mathcal{E}) < 1$, and this is what determines the selective nature of the partitioning solution. Let us examine (A.4). If we neglect the off diagonal

element $V_{m\ell}$ with respect to $(\gamma_{m\ell}+\gamma_{qm})^{\frac{1}{2}}$, (A.4) may be replaced by

$$\gamma_{q\ell}\gamma_{qm} \simeq 0 \qquad (A.5)$$

which means that either factor is zero. Hence,

$$\mathcal{E}_q \simeq E_j^o + V_{jj}^o \simeq E_j'$$

is the approximate value for which $\mathcal{E}_{iq}'$ blows up.

As $E_j^o + V_{jj}^o$ is an approximation, given by first order perturbation theory, to the eigenvalue E_j' of the secular equation we may expect that the eigenvalues E_k', $k \neq q$ are close to the points at which $\mathcal{E}_{1,q}$ blows up, and indeed this is what happens. From reference [92], we obtain the following results.

Eigenvalues of secular equation for He atom, using the configurations $(1s)^2$, $(s)(2s)$ and $(2s)^2$ as a basis (unscaled):

$$E_o' = -2.830996$$

$$E_1' = -1.956968$$

$$E_2' = -0.697606 \quad .$$

Values of $\mathcal{E}$ that make $\mathcal{E}_{1,q}'$ blow up:

For q = 0:	-2.036792,	-0.698778
For q = 1:	-2.750939	-0.69828
For q = 2:	-2.830438	-1.9559134

For comparison we give the first order perturbation energy approximation: $E_q' \simeq E_q^o + V_{qq}^o$:

E'_o -2.750000

E'_1 -2.036351

E'_2 -0.699219 .

This simple study of the convergence of the iterative procedure gives us the conditions under which we may expect $\mathcal{E}'_q$ to converge to $E'_q = f(E'_q)$ and not to any other root of the secular equation E'_K. More details are given in reference [92].

APPENDIX II

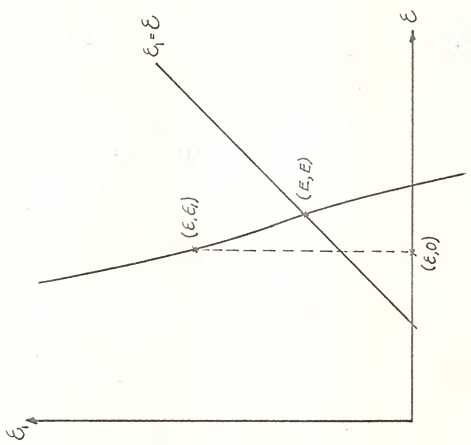

Fig. 1. Bracketing Theorem

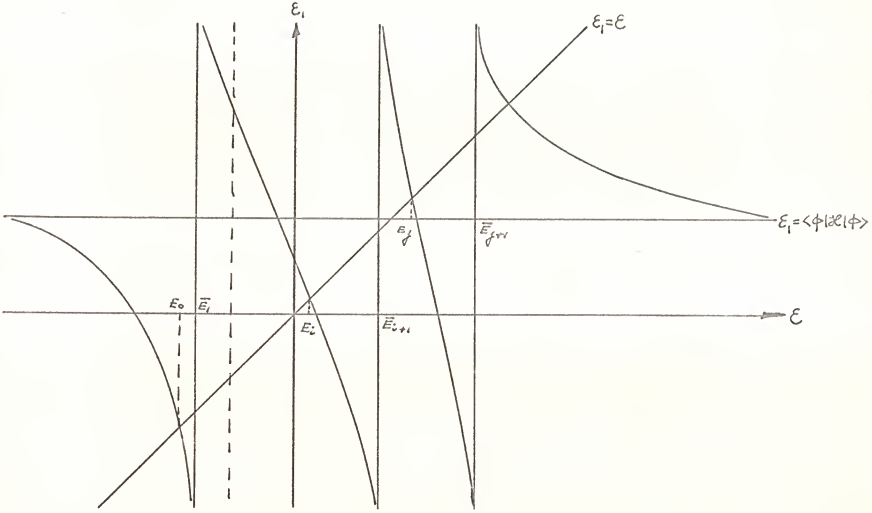

Fig. 2. Bracketing Function

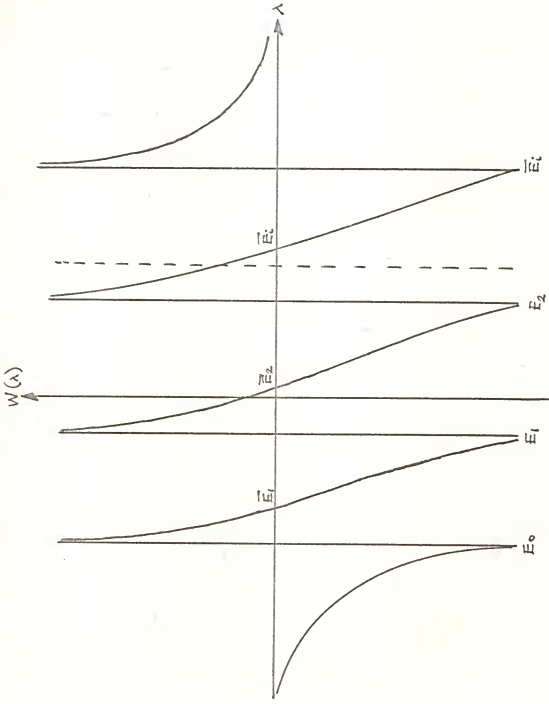

Fig. 3. Weinstein Function

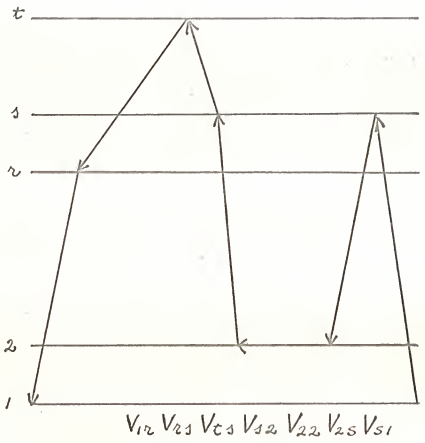

Fig. 4. Typical Term in Brillouin-Wigner Series

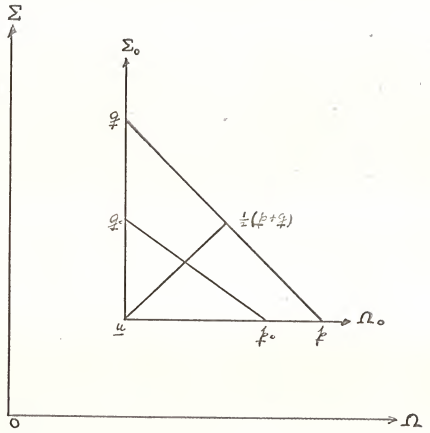

Fig. 5. Reciprocal Variational Problems

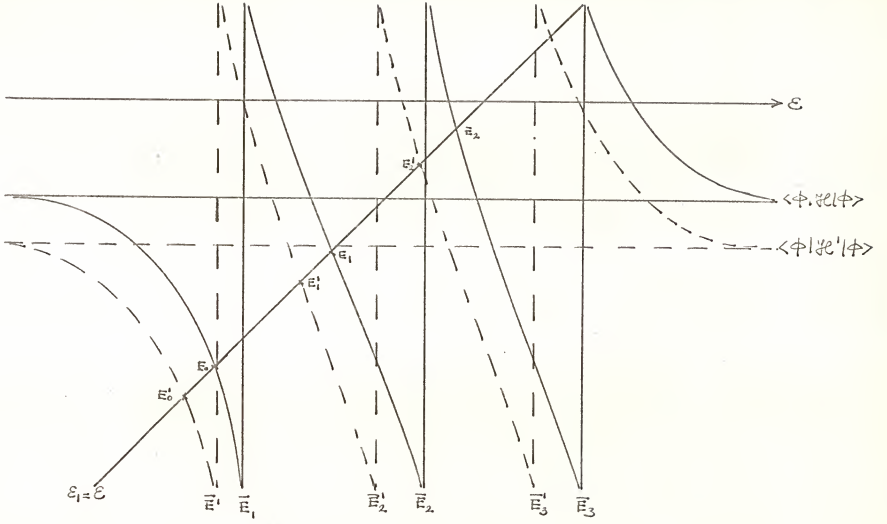

Fig. 6. Partitioning Function for Truncated T_0

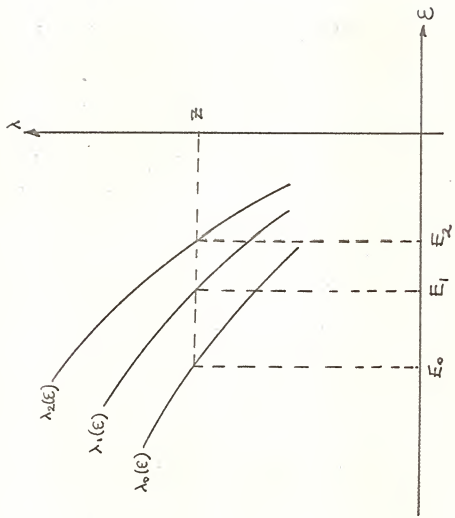

Fig. 7. Eigenvalue Relation $\lambda(\mathcal{E})$

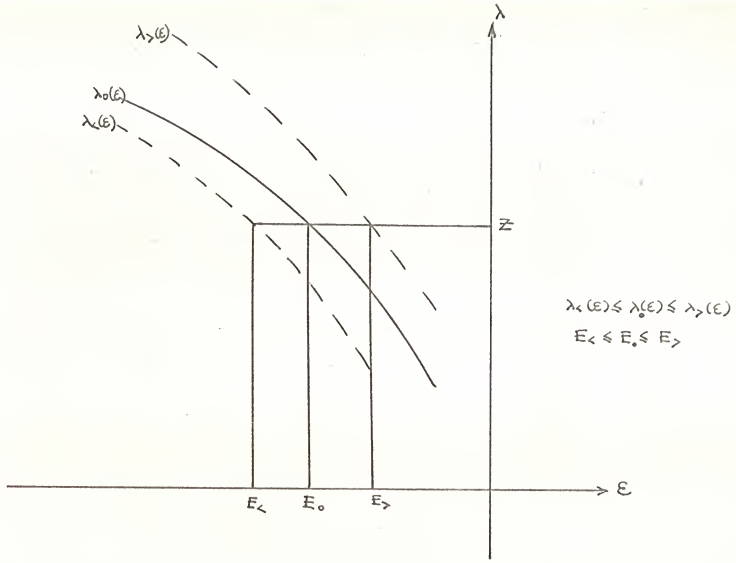

Fig. 8. Upper and Lower Bounds to $\lambda(\varepsilon)$

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BIOGRAPHICAL SKETCH

Saul Osvaldo Goscinski was born in Buenos Aires, Argentina on October 29, 1938.

In December, 1956, he graduated from the Colegio Nacional de Buenos Aires and in December, 1961, from the University of Buenos Aires, with the degree of Licenciado en Química. He enrolled at the University of Florida to pursue graduate studies in chemistry on February, 1962, and was a member of the Quantum Theory Project since then, with the exception of the summers of 1962 and 1963 which he spent at the Theoretical Chemistry Institute in Madison, Wisconsin, and the summer of 1965 which he spent at the Quantum Chemistry Group in Uppsala, Sweden.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April 23, 1966

E. Reed Jones

Dean, College of Arts and Sciences

Dean, Graduate School

Supervisory Committee:

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